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FATE OF RADIOACTIVE CONTAMINANTS IN WATER

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Robert A. Taft Sanitary Engineering Center

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FATE OF RADIOACTIVE CONTAMINANTS IN WATER

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Progress Report No. 2
For the Period May 1, 1958 to June 30, 1959

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Bureau of State Services
Division of Radiological Health
Robert A. Taft Sanitary Engineering Center
Cincinnati 26, Ohio

1960

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SUMMARY

This report on water-borne radionuclides records progress made in five specific areas of study during the second year of the project—covering the period from May 1, 1958 to June 30, 1959. The areas covered include instrumentation, tritium, estuarine and marine waters, aquatic biota, and the fate of radioactive materials in the water environment.

The first section describes additions to the counting room during the past year and describes some of the changes made in existing equipment to improve sensitivity. Data are presented on instrument calibration and spectra are shown for specific radionuclides.

In the section on tritium, reference is made to progress being made to improve optics and obtain more sensitivity in the analysis. Results of tritium analyses are reported in Section V.

Improvements made in the analyses of sea water for gross activity and for specific radionuclides are noted in Section III. Methods were developed for the identification of cesium, iodine, and other radionuclides and are reported.

Section IV describes the methods used to identify radionuclides associated with specific samples of filamentous algae collected at the Savannah River Project site.

The data obtained in the analysis of laboratory and field samples collected at KAPL are reported in Section V. Some data are presented also on Savannah River and Shippingport samples. Experiences in the development of a stream sampling device are also described.

FATE OF RADIOACTIVE CONTAMINANTS IN WATER

Progress Report No. 2

I. INSTRUMENTATION

Gerald J. Karches and Byron M. Branson, Physicists

1. INTRODUCTION

In order to fulfill the work under contract from the Atomic Energy Commission, some new equipment has been added, sensitivity improvements made on others, and an expansion of the physical facilities has been completed. The new instrumentation includes three compact single-channel gamma spectrometers, and one automatic scanner and ratemeter for an analyzer.

2. COUNTING ROOM

Because of the very crowded conditions of the counting room described in our previous report (1), the area was extended to double its size and the instrumentation relocated. One new wall, similar to the previously constructed walls, completed the addition. Two of the walls of the area are external walls of the building basement, of heavy poured concrete, in contact with the earth, and three floors under ground. A dual door 48" wide, required for access to the room with large equipment, is the only weak spot in the shielding.

The utilities provided are electricity and air conditioning. The electrical supply is a new source consisting of three separate 110-volt lines with a total capacity of 180 amperes. This room is illuminated with fluorescent lighting, since the liquid scintillation equipment is in the original room. The eight-ton air conditioner (mistakenly reported as a 3 ton unit in the initial report) now serves both rooms. The small wall exhaust fan was moved from the end wall to the end of the room farthest from the entrance. The rest of the room is constructed and equipped in a manner similar to that used in the original room.

3. LOW LEVEL (ANTI-COINCIDENCE) BETA COUNTER

Two more detector units have been added to the low background beta counter (1), doubling its counting capacity. By stacking the two units one over the other we saved 72 steel bricks and valuable space. Two-inch diameter detectors have replaced the 1" diameter G-M units originally provided.

By using shims to bring the sample closer to the detectors our counting efficiency for Y^{90}, spread evenly over a 2" planchet, has been increased to 42 per cent. This is almost a three-fold increase in efficiency over the first set-up, and the background is still less than 1 cpm.

4. SINGLE-CHANNEL GAMMA ANALYZERS

Three single-channel analyzers were purchased for use with tracer levels of activity, thus freeing the multichannel analyzers for measuring the low levels of activity in environmental samples.

Two of the single channel analyzers (Figure 1) are coupled to 2" NaI crystals for studies of the rate of uptake of Sr^{85} and Cs^{137} in fish. Both have been calibrated for these two isotopes and corrections made for interferences when both are present at the same time.

The other single channel analyzer (Figure 2) is intended to be used with a liquid scintillation counter designed to operate with one photomultiplier tube with no cooling. This arrangement will be satisfactory for higher energies or higher levels of activity.

We also have in use an automatic scanner (Figure 3) coupled to a single channel analyzer which scans the full energy range in time increments of 5, 10, 20, 40, and 80 minutes. With ten different chart speeds, the instrument is quite versatile. The scanner also automatically resets and starts scanning again, if wanted, making the instrument adaptable for decay studies.

5. 100-CHANNEL GAMMA SPECTROMETER

The response of the gamma scintillation spectrometer combination described in Technical Report R59-2(1), to the nuclides Mo^{99}, Ce^{141}, I^{131}, Au^{198}, Ru^{103}-Rh^{103}, Zn^{65}, Co^{60}, and K^{40} has been determined. Many of the above have been calibrated by 4-pi counting. An efficiency curve of gamma energy vs. efficiency of detection under the photopeak is shown for both the 2" and 4" solid NaI crystals. These efficiency values are derived by summing the

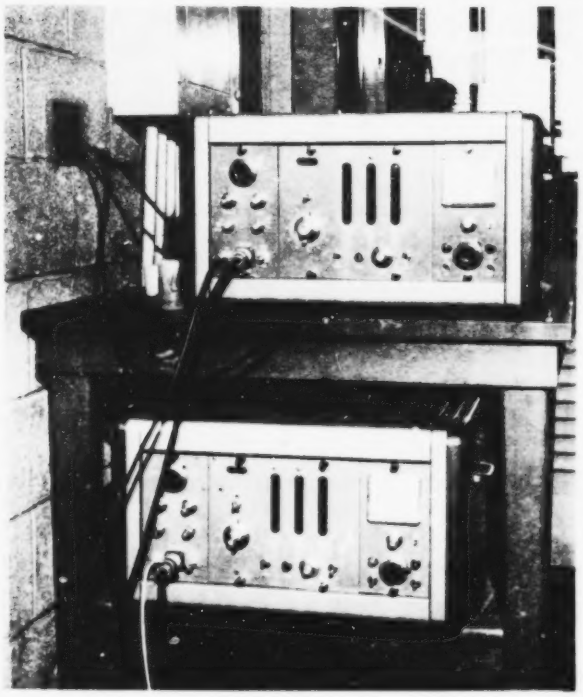

Figure 1. SINGLE CHANNEL GAMMA SPECTROMETER

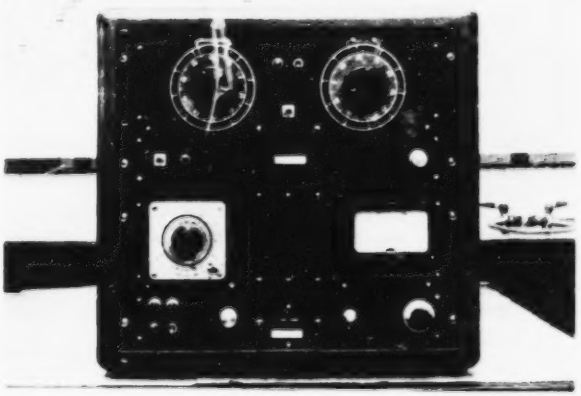

Figure 2. SINGLE CHANNEL PULSE HEIGHT ANALYZER

channels in the photopeak, for a count per minute value, and dividing by the number of photons of that energy emitted per minute (Figure 4).

Spectral curves for Cs^{137} are shown for both the 2" and 4" crystals in Figure 5. It should be noted that the peak-to-Compton ratio in the larger crystal is 9 to 1, while for the 2" it is about 5 to 1, indicating more of the gammas are completely absorbed inside the 4" crystal. The greater value of the large crystal for determining low levels of activity is clear. Samples were not of the same activity and consequently the peak heights are not to be compared directly. Spectra for I^{131}, Ru^{103}-Rh^{103}, Ru^{106}-Rh^{106}, Zr^{95}-Nb^{95}, Ce^{144}-Pr^{144}, Zn^{65}, and Co^{60} on the 4" crystal are also shown. All nuclides were in

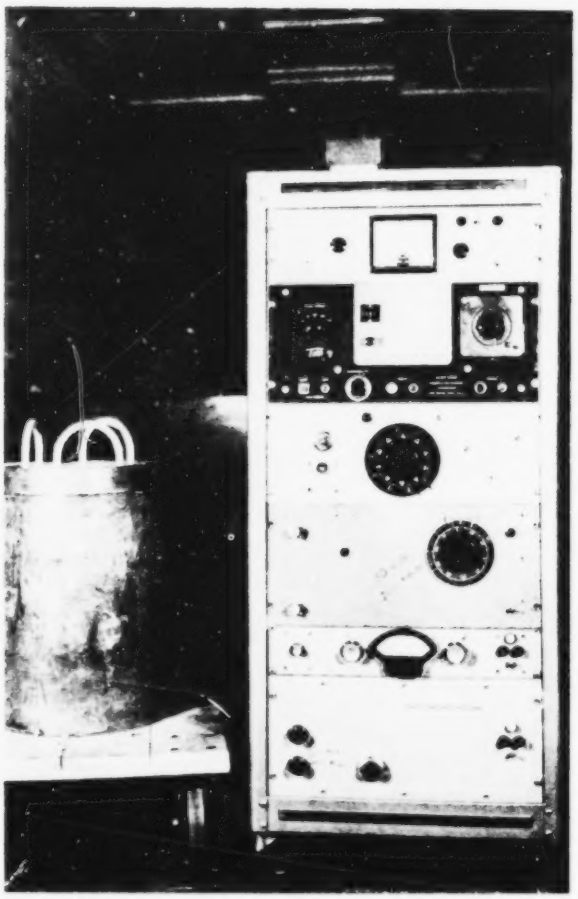

Figure 3. SINGLE CHANNEL ANALYZER WITH AUTOMATIC SCANNER

the form of point sources in dishes. It may be pointed out that the 637-kev peak in the I^{131} spectra (Figure 6), would interfere with the Cs^{137} photopeak quite seriously if they were in the same sample, as is often the case in milk samples. The effect is especially pronounced when there is a large amount of I^{131} in relation to the Cs^{137} level.

Figure 7 shows spectra for Ce^{144}-Pr^{144} and Zr^{95}-Nb^{95} both of which are commonly found in environmental samples. Although the Ce^{144}-Pr^{144} spectrum has a 696-kev photopeak, for all practical purposes this is never "seen" because of its relatively low abundance and also since it is usually masked by Cs^{137} and Zr^{95}-Nb^{95}.

Both the Ru-Rh spectra (mass numbers 103 and 106 given in Figure 8 have peaks at about 500 and 620 kev but the ratios are quite different, enabling a distinction to be made between these two. The 1150 kev peak of Ru^{106}-Rh^{106} is usually not "seen" in environmental samples because of its low abundance.

Figure 9 gives spectra of Zn^{65} and Co^{60}. Although they are not fission products they nevertheless are found in environmental samples as a result of neutron activation.

The low level gamma spectrometer has also been calibrated for samples of various volumes and different gamma energies (Table 1). As a result, quantitative reporting of the I^{131}, Cs^{137}, Ba^{140}, and K^{40} content of fluid milk is now possible. The necessary correction for the mutual interference of these isotopes has been accomplished by solving a series of simultaneous equations. This method is in the process of publication (2).

6. REFERENCES

1. Straub, C. P., and A. S. Goldin, Fate of Radioactive Contamination in Water, Progress Report No. 1 (For the Period April 7, 1957 to May 1, 1958). Report SEC TR R59-2, Robert A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio.

2. Hagee, G. R., G. J. Karches, and A. S. Goldin, Determination of I^{131}, Cs^{137}, and Ba^{140} in Fluid Milk By Gamma Spectroscopy. Division of Radiological Health, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

Table 1. EFFICIENCY OF GAMMA DETECTION

Nuclide	Gamma energy in kev	Sample size in liters	Efficiences in %
Cs^{137}	662	1	8.0
Cs^{137}	662	2	6.1
Cs^{137}	662	3.5	4.4
Ba^{140}-La^{140}	1620	1	2.8
Ba^{140}-La^{140}	1620	2	2.2
Ba^{140}-La^{140}	1620	3.5	1.6
I^{131}	364	3.5	6.3
K^{40}	1420	3.5	2.8

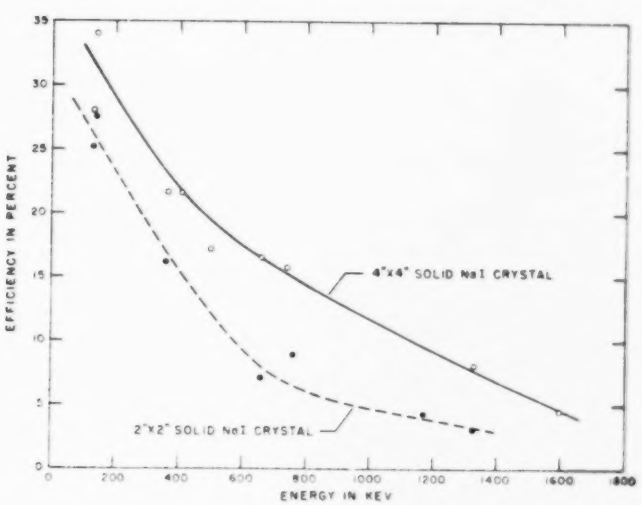

Figure 4. DETECTION EFFICIENCY AS A FUNCTION OF PHOTOPEAK ENERGY – POINT SOURCE

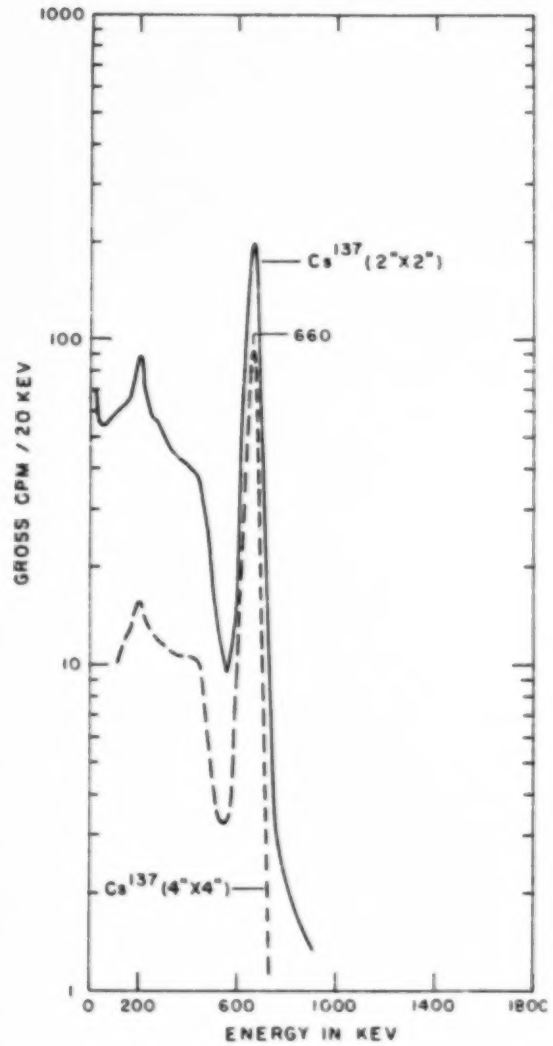

Figure 5. CESIUM-137 GAMMA SPECTRUM. NaI POINT SOURCE.

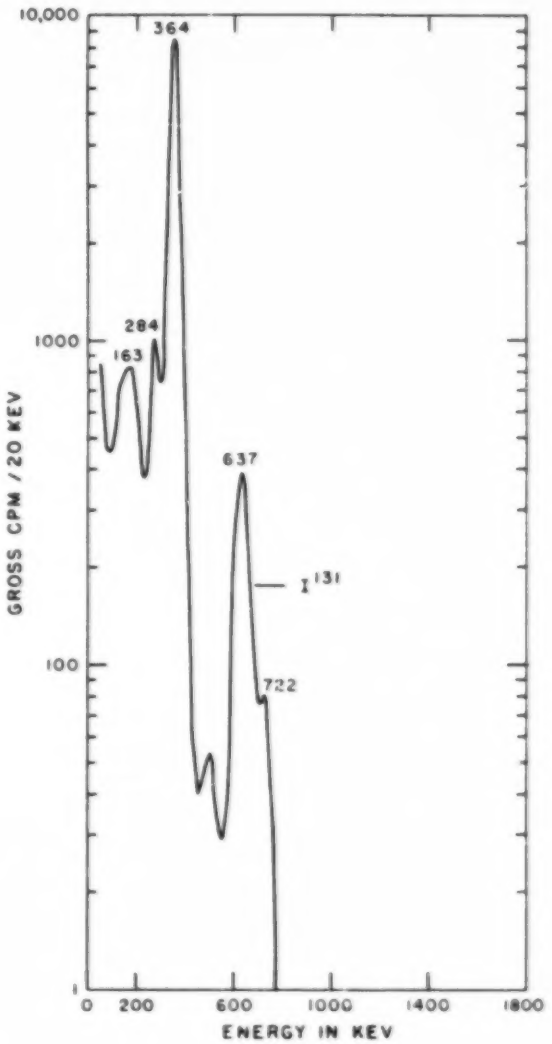

Figure 6. IODINE-131 GAMMA SPECTRUM. 4" x 4" SOLID NaI POINT SOURCE.

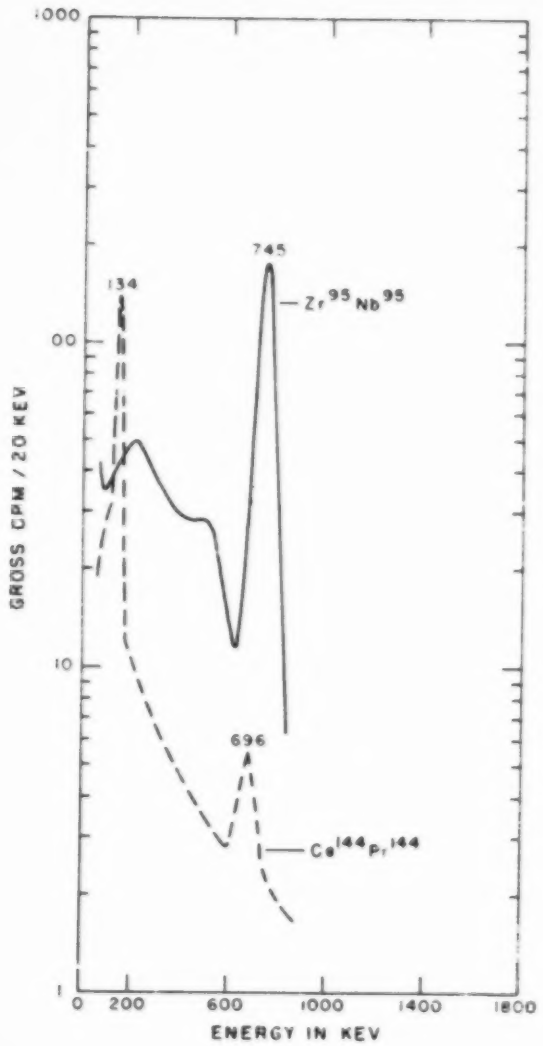

Figure 7. ZIRCONIUM-95-NIOBIUM-95 AND CERIUM-144 - PRASEODYMIUM - 144 SPECTRA. 4" x 4" SOLID NaI POINT SOURCE.

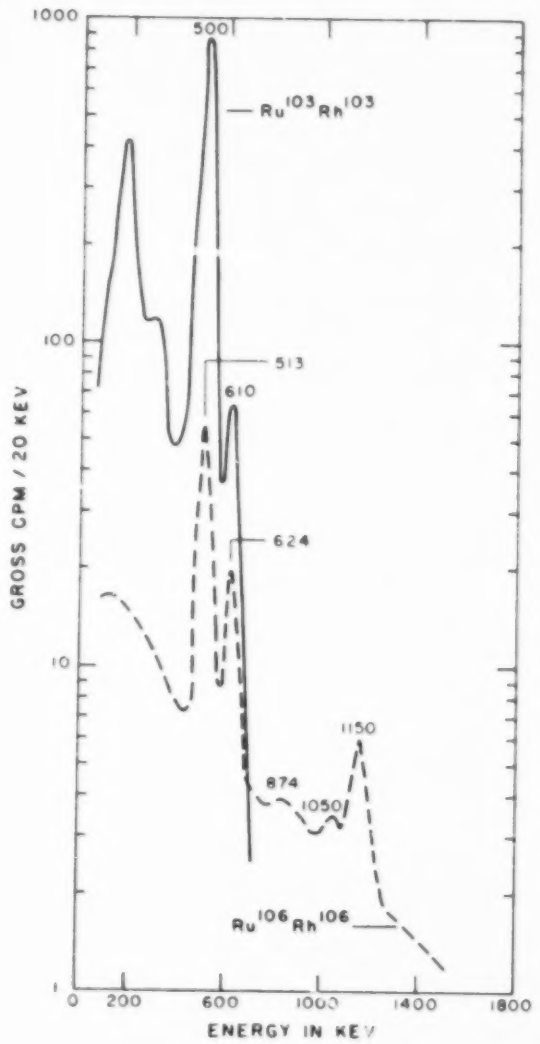

Figure 8. RUTHENIUM-103-RHODIUM-103 AND RUTHENIUM - 106 - RHODIUM - 106 SPECTRA. 4" x 4" SOLID NaI POINT SOURCE.

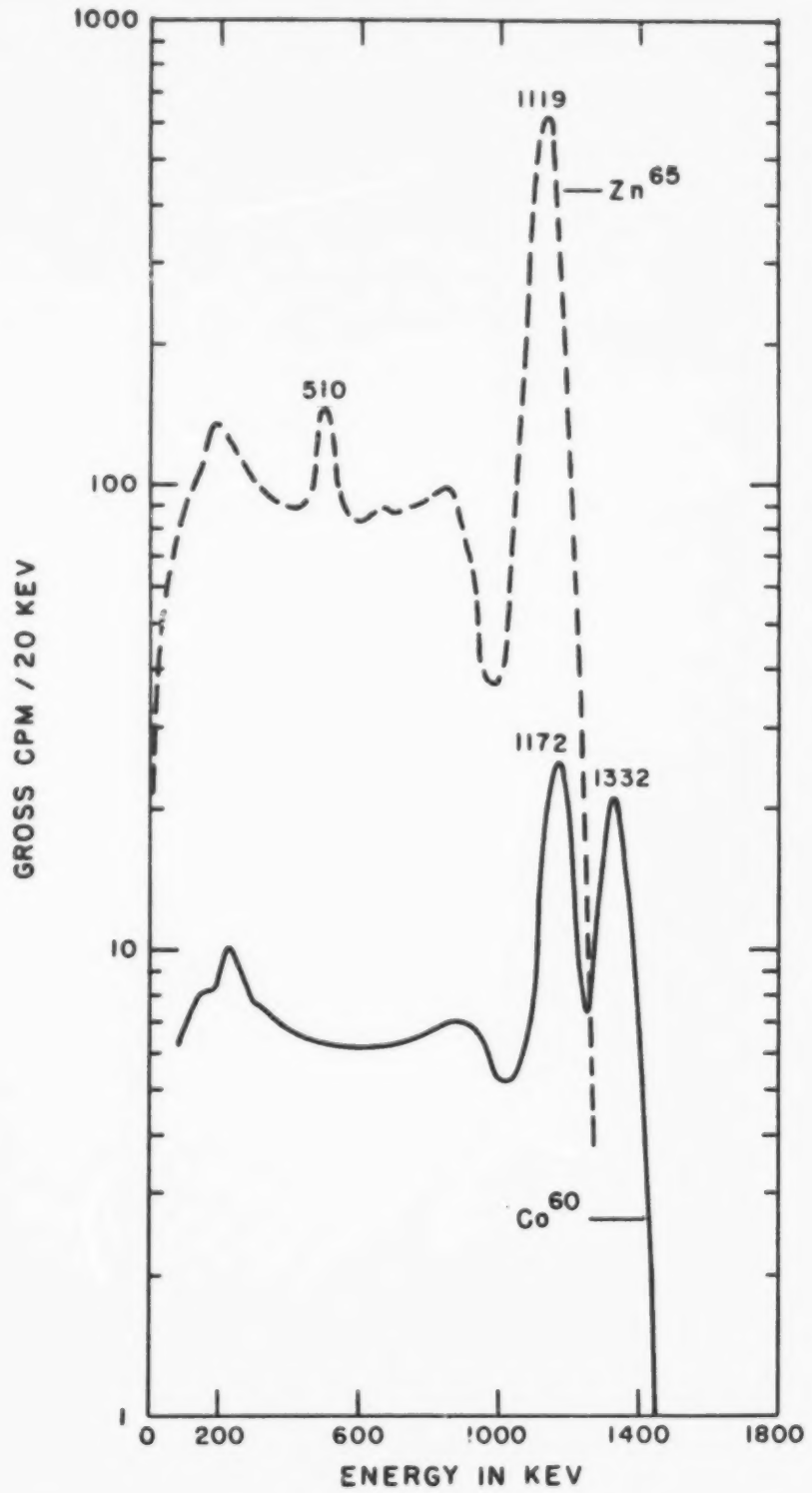

Figure 9. ZINC-65 AND COBALT-60 SPECTRA. 4" x 4" SOLID Na POINT SOURCE.

II. TRITIUM

Vincent J. Sold, Chemist

1. INTRODUCTION

Tritium analyses have been made on samples obtained from the Shippingport, Pennsylvania area, since this nuclide is formed by neutron irradiation of lithium in the primary coolant of the PWR at that site. Because tritium, an isotope of hydrogen, cannot be removed readily from water solutions, and because it cannot be stored for decay (half-life over 12 years), it is diluted and discharged to the Ohio River. The State of Pennsylvania has agreed to permit an average daily discharge of 10 curies of tritium with a maximum of 50 curies in any one day. This high rate of discharge, much greater than that allowed for any other radionuclide, is permitted because of the relatively low radiotoxicity of this nuclide.

The project has a two-fold purpose; 1) to develop and evaluate methods for the routine analysis of tritium in water at levels well below the MPC; and 2) to study the effect of tritium on assay procedures presently used in radiological analyses.

2. PRIOR WORK

The historical development of tritium analysis was summarized in SEC Tech. Report R59-2(1). Very briefly, because of the extremely low energy of the tritium beta radiation, specialized equipment is necessary for its counting. Either internal-sample gas-phase counters or liquid scintillation counters may be used for the counting of tritium at moderately, but not extremely, low levels. Determinations at low levels of activity are further complicated by the difficulty of concentrating tritium in water samples. Although it is somewhat less sensitive, the liquid scintillation technique was chosen because sample preparation requirements are much less stringent.

During the period covered by the previous report (1), conditions for counting tritium in water were established and preliminary calibrations were determined.

3. METHODS

The sample preparation procedures established for counting tritium permitted the solution of 4 ml of water sample in 16 ml of scintillation solution. The efficiencies obtained at various times were 3.9, 4.0, 3.4, and 2.6 per cent (1).

Although considerable effort has been expended, the cause for the variability in efficiency has not been elucidated. Rigorous purification of the solvents used in the "611" solution—1,4-dioxane; anisole; and 1,2-dimethoxyethane—by distillation of the commercially available materials has not solved this problem, either in the attainment of high efficiencies or of consistent efficiencies. Some of the variations and very high values initially obtained in counting efficiency, are attributed to instrument malfunction.

After maintenance of the liquid scintillation spectrometer for optimum operation, the following precautions have been taken to assure the validity of analytical work.

a. Freezer temperature has been raised to just above 0°C.

b. All solvents used in tritium assays are distilled for further purification of the commercially available material.

c. Fresh "611" solution is prepared for each group of samples and stored in the cold until used. Older solutions have on occasion given high background counts.

d. All samples for tritium analysis are distilled in order to avoid the possibility of color quenching or light absorption by organic or suspended solids. This also eliminates interference by other radioactive materials in the tritium determination.

e. The counter efficiency and background are determined individually for each set of measurements by counting a known tritiated water standard and a known distilled water.

The complete analytical procedure for tritium follows:

A 15-20 ml portion of the water sample is distilled to dryness to remove dissolved and particulate matter which could absorb the light emitted by the scintillator or "quench" in some other manner, and also to separate non-volatile radioactive materials.

Four ml of the distillate is mixed with 16 ml of "611" scintillation solution in a 5 dram Crystal Lite Vial (2,3), cooled and counted in the Packard Tri-Carb liquid scintillation spectrometer. Standard tritium and background samples are prepared and counted simultaneously to nullify errors produced by aging of the scintillation medium or long term instrumental drift.

Freshly prepared "611" scintillation solution (2) consisting of:

6 parts 1,4-dioxane (by vol)
1 part anisole (by vol)
1 part dimethoxyethane (by vol)

PPO (2, 5-diphenyloxazole) 15 g/l
POPOP (1, 4-di 2-(5 phenyloxazolyl) benzene)
0.62 g/l

is used for tritium determinations. All of the solvents are distilled to insure purity since small amounts of contaminants could have a significant effect on scintillation counting.

Wheaton glass vials, No. A-3305, are used as our sample containers (2, 3). Note 1: Distillation to dryness insures complete transfer of the tritium from the residue to the distillate. It is believed that tritium may concentrate in the residue if only a portion is distilled. Note 2: Recently, samples of the Wheaton Company's 300-1, 5 dram Low Potassium Vial were obtained. This new bottle is being evaluated.

Table 2 gives the counting efficiencies and backgrounds obtained at various times during the year, from which minimum detectable concentrations have been calculated.

Performance of the liquid scintillation spectrometer could be improved with better optical coupling between the sample and the tubes. This is apparent from theoretical considerations and has been reported (4)

Preliminary work has been carried out on such improved optics, but whether this will lead to significant improvement is not yet known. A better scheme for selecting photomultiplier tubes is also under study. These steps should allow some additional improvement in tritium counting efficiency and background.

The efficiency for counting tritium in the form of toluene is around 20-25 per cent which is more than ten times the efficiency for counting it in the form of water. This makes the exchange of tritium from water samples with the hydrogen of toluene, as has been done in Israel (5), attractive as a means of lowering the minimum detectable activity.

It may be mentioned that the maximum permissible concentration of tritium in water for occupational exposure (168 hour week) (6) is 3×10^{-2} μc/ml or about 70,000 dpm/ml. Thus at the present efficiency level, much less than 1/1000th of this activity can be detected.

4. MEASUREMENTS

Measurements for tritium levels are reported under Shippingport in Section V, Fate of Radioactive Material.

5. FURTHER WORK

Further work in the development of liquid scintillation techniques for the measurement of tritium is primarily in two directions. First is the improvement of the instrumentation, primarily by application of better optics, but also through greater instrument stability and lower noise levels; and second is the application of sample preparation techniques to lower levels, by the use of larger samples and the application of chemical exchange methods.

6. REFERENCES

1. Straub, C. P., and A. S. Goldin, Fate of Radioactive Contaminants in Water, Progress Report No. 1 (For the Period April 7, 1957 to May 1, 1958). Report SEC TR R59-2, Robert A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio.

2. Davidson, J. D., and P. Feigelson, Practical Aspects of Internal-Sample Liquid Scintillation Counting, Intern. J. Appl. Rad. and Isotopes, 2 (1), 1-18 (1957).

3. Five dram Crystal Lite Vial, No. A-3305, T. C. Wheaton Co., Millville, New Jersey.

4. Horocks, D. L., and M. H. Studier, Low Level Plutonium-241 Analysis by Liquid Scintillation Techniques, Anal. Chem., 30: 1747 (1958).

5. Avinur, P., and A. Nir, Tritium Exchange Between Toluene and Aqueous Sulfuric Acid, Bull. Res. Council Israel, 7A: 74 (1958).

6. National Bureau of Standards Handbook 69, Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure, National Bureau of Standards, Department of Commerce, U. S. Government Printing Office, Washington 25, D. C. (June 5, 1959).

Table 2. COUNTING DATA, TRITIUM*

Date	Counting efficiency, per cent	Background cpm	Minimum Dectectable Activity, dpm/ml for counting-time of-		
			50 min	100 min	1000 min
6-11-58	1.74	118.7	62	44	14
7-21-58	2.20	71.4	38	27	8.5
10-25-58	2.39	77.1	36	25	8.1
5-1-59	1.40	67.6	58	41	13

* For 4 ml water sample in 16 ml "611" solvent; HV Tap 8, channel 10-100.

III. ESTUARINE AND MARINE WATERS

Richard J. Velten and Vincent J. Sodd, Chemists

1. INTRODUCTION

The objectives of this project have been described in the last progress report (1). Briefly, they may be summarized as the development of methods for the determination of gross radioactivity and of specific radionuclides in water of high salt content, and the study of the possibility of utilization of off-shore waters for the disposal of radioactive wastes.

Interest in the effect of radioactive materials on both estuarine and marine environments is extremely high because of the utilization of nuclear energy in ship propulsion, the possibility that radioactive waste from reactors will reach the sea, and increasing concern with the effects of the disposal of packaged wastes at sea. Two recent National Academy of Science reports (2, 3) have promulgated a better and more complete understanding of the use of coastal waters for waste disposal.

2. PRIOR WORK

A. Gross Activity

The determination of gross radioactivity in salt waters by evaporation has been limited to samples whose activity is high enough to permit use of very small samples (not over 10 ml) Somewhat larger samples, up to about 250 ml, have been used in a technique in which calcium carbonate is precipitated, carrying some 75 to 80 per cent of mixed fission product activity. In an earlier report (1), a sulfide screening technique was outlined.

B. Radionuclide Analyses in Sea Water

Difficulties in the radionuclide analysis of sea water arise primarily with the alkaline earth and alkali metals, since the bulk of the sea water cations are included in these groups. As a rule, sea water anions (mainly chloride) do not interfere although the sulfate content may give some difficulty in the analysis of barium or radium.

In the determination of strontium, it was found that carbonate precipitation did not quantitatively recover strontium under conditions such that magnesium remained in solution. Accordingly, the precipitation was carried out under more alkaline conditions, following removal of the magnesium by precipitation with 8-quinolinol at pH 7.

3. ANALYTICAL METHODS

A. Gross Activity

In general, method evaluation consisted of a study of the results obtained with NaOH-thioacetamide, NH_4OH-thioacetamide, and NH_4OH - H_2S. Furthermore, since the sulfide precipitates do not contain the alkaline metals, the alkaline earth metals, or some of the anions, particularly iodine, further work was done on the recovery of such materials from the supernatant after removal of the sulfide precipitate.

1. NaOH-Thioacetamide

Various tracers typical of different chemical groups were used to evaluate this precipitation techneque. These tracers—chromium-51, neodymium-147, ruthenium-106-rhodium-106, zirconium-95-niobium-95, and cerium-144-praseodymium-144—were added individually to liter samples of substitute sea water (4). Carrier lanthanum, iron, cobalt, zinc, nickel, cesium, and strontium were added; the solution was acidified, boiled to expel carbon dioxide, and made alkaline with sodium hydroxide. Thioacetamide solution was then added and the solution heated to promote hydrolysis of this reagent. After collection, washing, drying, and weighing, the precipitate was dissolved in HCl-HNO_3 and gamma counted under the same conditions as the controls. Tracer recovery results are given in Table 3. The precipitate was quite large, about 1.25 grams. In all probability, this large quantity is due mostly to precipitation of magnesium hydroxide. Since there would be excessive self-absorption losses in beta counting such a large mass, the resulting poor efficiency would seriously hamper sensitivity at the desired low environmental levels.

2. NH_4OH-Thioacetamide

Because of the large mass of precipitate obtained with NaOH-thioacetamide, ammonium hydroxide was substituted as a base. The same procedure was repeated except that a test with zinc-65 tracer was added while neodymium-147 tracer was eliminated. The recoveries of the added tracers in the NH_4OH-thioacetamide system are also summarized in Table 3. By this procedure, about 180 mg of precipitate was obtained. While this is not exactly the expected theoretical weight, the amount is satisfactory for beta counting. Some difficulty was noted

Table 3. RECOVERY OF TRACERS

Tracer	Recovery, per cent		
	NaOH Thioacetamide	NH_4OH Thioacetamide	NH_4OH H_2S
Cr^{51}	> 99	97	97
Ru^{106}-Rh^{106}	> 99	98	95
Zr^{95}-Nb^{95}	99	95	93
Ce^{144}-Pr^{144}	> 99	99	95
Nd^{147}	> 99		
Zn^{65}		94	99.9

in this procedure, probably due to loss of NH_3 during the heating required to hydrolyze the thioacetamide. Unless considerable excess NH_4OH is used, the solution may become somewhat less basic than desired, which may account for the incomplete recovery of zinc, for example.

3. NH_4OH-H_2S

In testing this procedure a liter of substitute sea water with added lanthanum, iron(III), cobalt, zinc, nickel, and strontium carriers, as well as cerium-144-praseodymium-144, chromium-51, zinc-65, ruthenium-106-rhodium-106 and zirconium-95-niobium-95 tracers, was acidified, boiled, made basic with excess ammonium hydroxide, and saturated with H_2S to complete precipitation. Following collection, washing and drying of the precipitate, the amount of activity remaining in solution was evaluated by gamma spectroscopy. The results are given in Table 3. Since relatively large amounts of zirconium-niobium remained in solution, there was interference in the determination of the three nuclides which have lower gamma energies (cerium-144-praseodymium-144, chromium-51, and ruthenium-106-rhodium-106). Accordingly, the procedure was repeated without the zirconium-niobium tracer. The recovery of the other radionuclides was then found to be greater than 99 per cent. Essentially quantitative recovery is thereby obtained for the following groups of elements: 1) transition elements—chromium, zinc, and cobalt; 2) noble elements—ruthenium and rhodium; 3) rare earths—cerium and praseodymium. Recovery of zirconium-niobium was not entirely satisfactory, amounting to about 93 per cent. Either the NH_4OH-thioacetamide or the NH_4OH-H_2S method appears feasible, according to which is most convenient.

While this method is excellent for screening "gross activity", the basic sulfide precipitate does not contain the alkaline earths, alkali metals, or iodine. These must be recovered by additional treatment. However, in most situations of interest such as reactor operations, fallout, discharge of primary coolants, etc., at least some of the isotopes involved will be detected by the basic sulfide procedure, which therefore is suitable for a screening technique. The only operations which would not be detected by such a procedure are those involving the use of pure radioisotopes of the alkaline earth, alkali metal, or some nonmetallic families, such as cesium-137, strontium-89, iodine-131, or tritium. Even utilization of strontium-90 would be detectable since the associated yttrium-90 could be detected.

The few remaining nuclides are identified by the techniques used in radionuclide determinations. Thus, the procedure used for strontium is suitable for the detection of gross strontium and barium, while the standard iodine procedure is directly applicable to salt waters.

The methods described herein have been prepared and submitted for publication in Analytical Chemistry (5).

B. Radionuclide Analyses of Sea Water

1. Strontium

The method for determination of strontium in sea water was described in report R59-2 (1) and has been published (6).

2. Cesium

The determination of cesium in salt water is complicated since the chloride content of the sea water interferes with the precipitation of ammonium cesium phosphomolybdate, commonly used in our cesium determination. However, a procedure based on the precipitation of silicotungstate (7) has been used. For this, either the original sea water, the supernate from basic sulfide separation, or the supernatant remaining from the removal of strontium, with cesium carrier, is concentrated to approximately one-third its volume and made 3 N in HCl. Any NaCl salting out is removed by centrifugation. The solution cooled to 10 C and silicotungstic acid added, is stirred for 15 minutes. The resulting precipitate is washed with cold 6 N HCl and dissolved in

6 N NaOH. Excess $HClO_4$ is added and the solution carefully heated to boiling to precipitate silicon and tungsten oxides. After these are removed, the filtrate is evaporated to fumes of $HClO_4$, cooled in an ice bath, and the chlorate precipitated by addition of cold absolute methanol (or cold absolute ethanol). The precipitate, after several washes with cold absolute alcohol to remove sodium and potassium, is mounted, and counted with either beta or gamma instrumentation.

3. Iodine

Iodine can be determined directly from sea water by adding NaI carrier, making the solution basic, preferably with sodium hydroxide, and heating with NaOCl to oxidize the iodine to iodate and periodate. Any material separating on addition of the base is removed. The solution is then made acid and the iodine reduced to iodide with $NaHSO_3$. The usual treatment with sodium nitrite and extraction with CCl_4 serves to separate and purify the iodine. Three or four extractions with CCl_4 are normally sufficient to remove substantially all the iodine. From the color of the successive organic extracts, the degree of removal can be estimated. The iodine is then back-extracted from the carbon tetrachloride with bisulfite and either determined by gamma counting of this back-extract or precipitated as silver iodide for beta counting.

4. Other Radionuclides

Other radionuclides are determined from the basic sulfide precipitate obtained as described for the gross beta determination. This sulfide precipitate, which contains the rare earths, zirconium-niobium, ruthenium, cobalt, manganese, zinc, iron, and similar elements, is first dissolved in acid and heated to drive off residual H_2S. The solution is then made approximately 10 per cent in HCl. H_3PO_4 is added, and the mixture digested warm to precipitate zirconium and niobium, which are then separated for counting. Excess phosphate is removed by the addition of inert zirconium carrier. The solution is concentrated and made approximately 7 N in HCl and iron is removed by extraction with ether. After this cobalt is removed by precipitation as the alpha-nitroso beta-naphthol derivative, rare earths as oxalates at pH 3, nickel as the dimethylgloxime compound from netural solution, manganese as MnO_2 from concentrated HNO_3 solution by addition of solid $KClO_3$, and finally zinc as sulfide from neutral solution. All of these fractions can be beta-or gamma-counted as appropriate. Although the method has not been rigorously tested, preliminary results indicate that zirconium and cobalt fractions are recovered quantitatively in pure condition and that recoveries of other materials are greater than 70 per cent in reasonably pure condition. For more specific information on this analytical scheme, see Section IV - Aquatic Biota.

The separation of metallic constituents by anion exchange, developed by Kraus at Oak Ridge National Laboratory and by the group at US Naval Radiological Defense Laboratory provides another approach which has been investigated for the determination of the transition elements. In the application to marine or estuarine waters, the first step is the separation of a basic sulfide precipitate. This precipitate is then dissolved in HCl and the solution brought to approximately 11 to 12 N with HCl. When this solution is passed through an anion exchange resin, such as Dowex-1(Cl) or Dowex-2(Cl), transition elements including chromium, manganese, iron, cobalt, copper, zinc, zirconium, and niobium are retained on the resin, while the rare earth elements, the alkaline earth elements, alkali metals, and nickel pass into the effluent. Various species on the resin can then be sequentially eluted, each with its specific concentration of HCl or HCl-HF. While the technique appears very promising and excellent preliminary results have been obtained, the exact conditions for the best separation and recovery are still under investigation, so that the detailed method cannot be given at this time.

4. RESULTS

No samples of estuarine or marine waters have been analyzed under this contract, since there is no regular sampling program for these materials. However, the methods have been used in a number of other applications, both at the Center and by outside agencies, with gratifying results. For example, in the surveillance program in the vicinity of the Portsmouth, New Hampshire Naval Base, where the gross activity of the sea water had formerly been reported as "less than 3,000 μμc/l", it is now reported in numbers in the range of 15 to 25 μμc/l. Similar results have been obtained in connection with surveillance operations in the Delaware River area where there are a number of saline water sampling stations and in the Hampton Roads, Virginia area. Radionuclide analyses have been made of strontium-90 in the Delaware River area, where the values obtained in saline water locations have been consistent with those obtained from fresh water locations. While this, of course, does not conclusively validate the methods, it constitutes strong presumptive evidence.

5. ACKNOWLEDGEMENT

In addition to the authors, the following have contributed substantially to the work reported in this section: Seymour Gold, James Gilchrist, and George W. Frishkorn.

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IV. AQUATIC BIOTA

Richard J. Velten, Chemist

1. INTRODUCTION

The study is designed to evaluate the uptake of radionuclides by aquatic organisms, both as it affects the food chain of man and as it may serve for monitoring the environment. Concentration of radionuclides by aquatic biota may make necessary drastic revisions in the disposal of wastes, particularly where the human food chain is involved (1). Since the study of fresh water and marine organisms involves the same techniques, both are considered here.

Because of the low levels of radioactivity, very careful chemical techniques are required, and extremely sensitive and sophisticated instrumentation must be evaluated for optimum detection capabilities.

2. PRIOR WORK

In previous years, most of the uptake information has been obtained from field operations in the Pacific, in connection with Proving Grounds activities. Most of these measurements were of gross activity with some consideration of specific radionuclide contamination. These groups have shown that the fission product strontium concentrates in gills, bone and shell, and integument rather than in the edible portion of sea foods. The induced radionuclides, such as zinc-65, cobalt-57/58/60, iron-55/59, and manganese-54, did concentrate in the edible portion of many marine species. The Fishery Radiobiological Laboratory, U.S. Fish and Wildlife Service, and the Hawaii Marine Laboratories have taken the lead in laboratory studies of radionuclide uptake by specific organisms.

3. ANALYTICAL METHODOLOGY

Standard radiochemical separations must be revaluated and modified. In environmental sampling the radionuclide sought must be chemically separated from both inert and radioactive impurities with high overall yield and purity. Because of the low levels of radioactivity present, large samples must be processed, while most of the classical separations are restricted to small sizes. These factors combine to make the problem difficult. Analytical techniques evolved from other activities of the Radiological Health Research Activities, Division of Radiological Health, SEC, have been investigated for adaptation to these analyses.

Techniques were developed using a filamentous algae specimen collected at Savannah River Project. The water from which this sample was taken showed very little activity, 50-75 $\mu\mu$c/l gross beta, with only ruthenium and zirconium-niobium detectable by gamma spectroscopy. The algae on the other hand showed large concentrations of a variety of radionuclides. The predominant nuclides originally observed in the gamma spectrum and confirmed in a second spectrum 90 days later were cerium-141/144, chromium-51, zirconium-95-niobium-95, zinc-65, cobalt-60, and ruthenium-103/106. These nuclides, plus manganese-54 and tantalum-182, were confirmed by subsequent radiochemical analyses. Neither cesium-134 nor cesium-137 which had been suspected were detected in the cesium fraction by gamma spectroscopy or beta counting. The scheme of chemical analysis with the gamma spectra of the

respective chemically separated fractions, is shown in Figures 10 to 18.

The alkaline-earth fraction was further examined to detect nuclides with no gamma emission. A purified strontium fraction was collected and beta-counted on an internal proportional counter. After the beta measurement, the voltage was lowered to the alpha detection region. Relatively large amounts of alpha activity were found. To confirm the presence of radium, barium carrier was added, separated from the strontium, and counted as barium sulfate after further purification. The alpha (radium) activity was found in this fraction. The rate of ingrowth of daughter activity (2) showed that the isotope present was radium-226. Both strontium-89 and strontium-90 were found in the strontium residue after barium separation.

The study was purely developmental and while some fractions are not chemically pure still they show the nuclides sought. Further work to improve these separations and recoveries is in progress. To date, experiments on added tracers have resulted in an improved iron separation by solvent extraction from hydrochloric acid instead of the basic acetate procedure. Better manganese recovery by precipitation of the dioxide in concentrated nitric acid with potassium chlorate has been achieved. Application of anion exchange techniques shows promise for separation and recovery of transition elements.

4. UPTAKE

Using strontium-85, preliminary laboratory investigations of the uptake of strontium by fish were begun.

A study of the concentration of trace stable elements from sea water by shellfish, based on neutron activation analysis of the shellfish and of the surrounding water, was initiated. Although samples have been collected and submitted to neutron bombardment, the analyses have not been completed.

5. FURTHER WORK

Future work includes development of a method for sequential analysis of many radionuclides in aquatic biota. With such a method, concentration factors for a variety of biota will be investigated by chemical and radioactivity assay of exposed biota, and also by activation analysis for trace elements. Emission spectroscopy also will be evaluated as an analytical tool.

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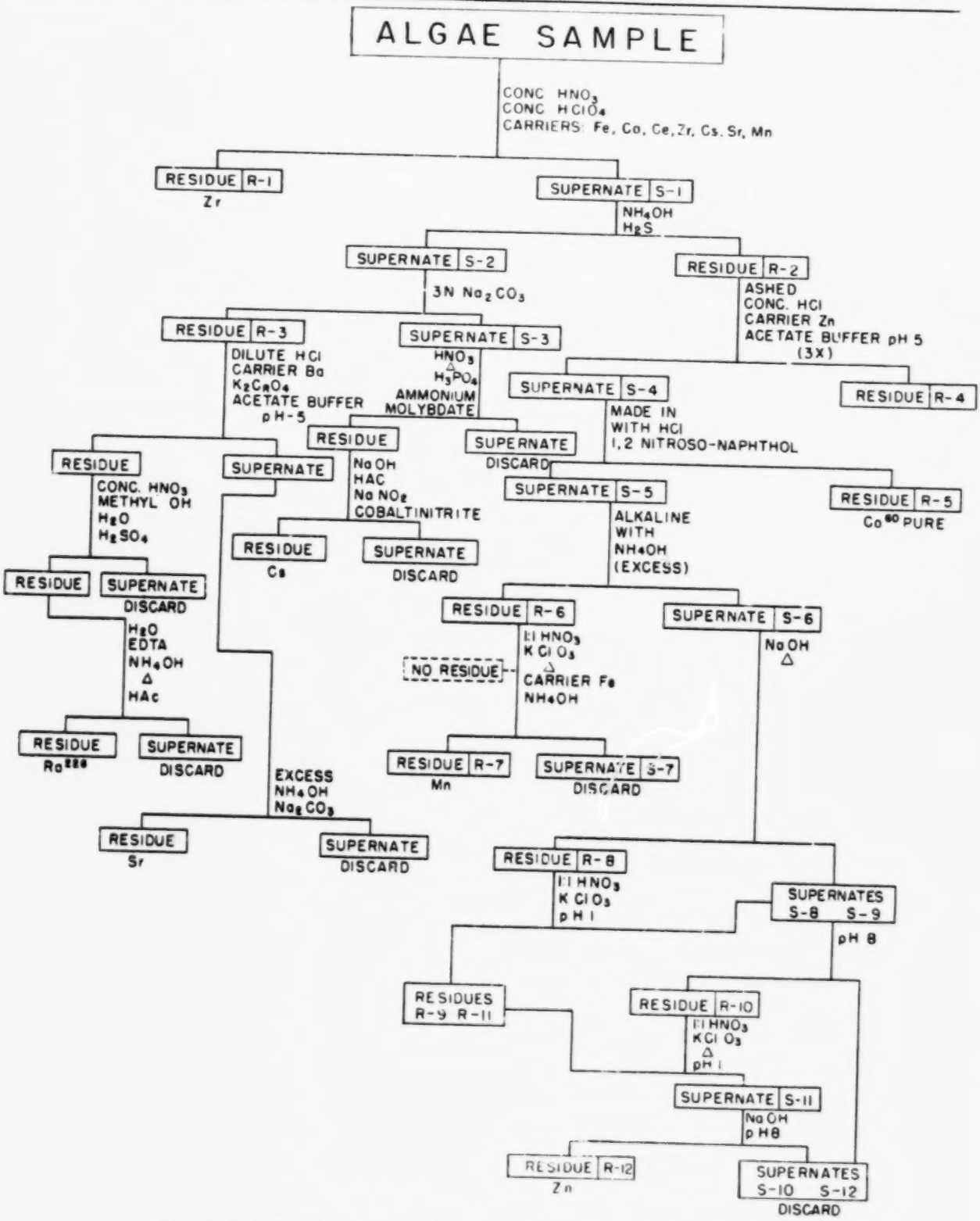

Figure 10. METHOD OF CHEMICAL TREATMENT OF ALGAE SAMPLE

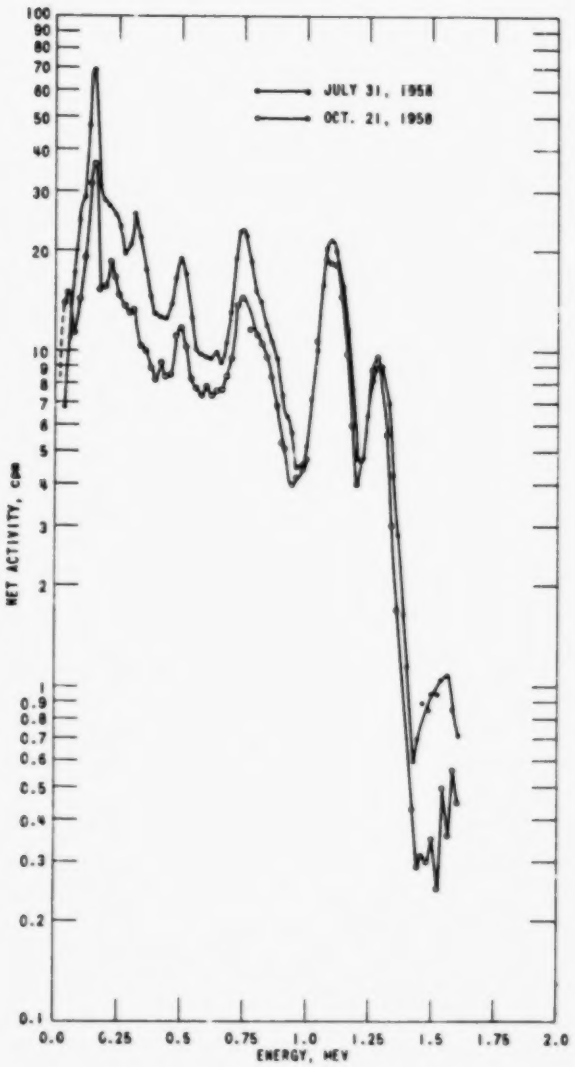

Figure 11. ALGAE DECAY CURVES

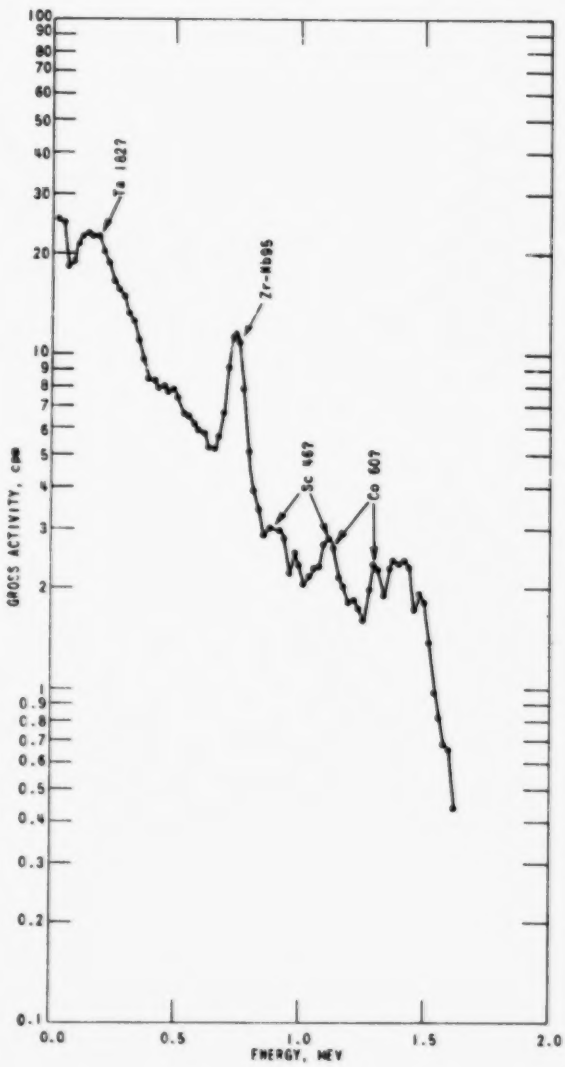

Figure 12. ALGAE FRACTION R-1

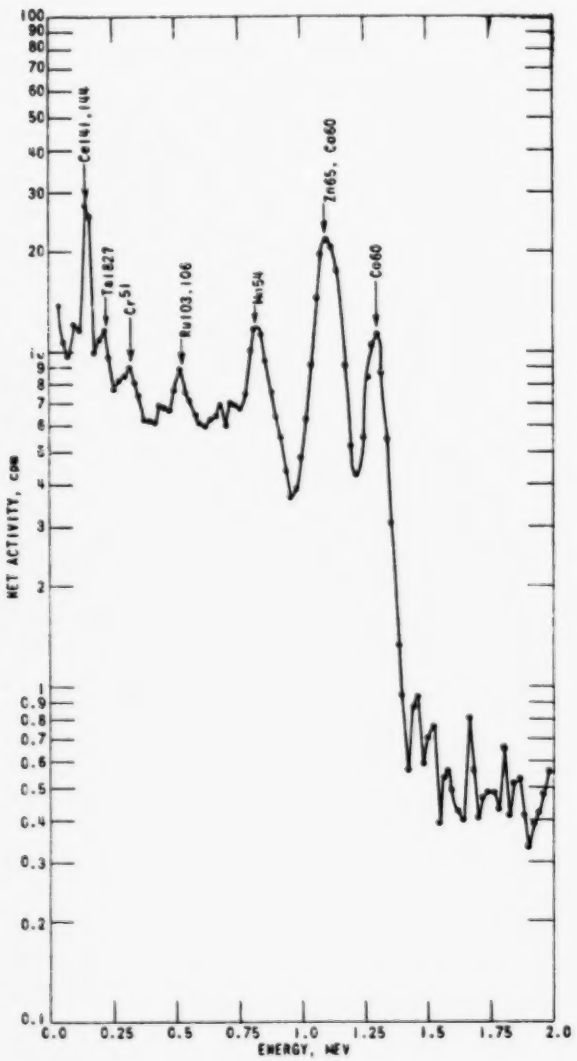

Figure 13. ALGAE FRACTION R-2

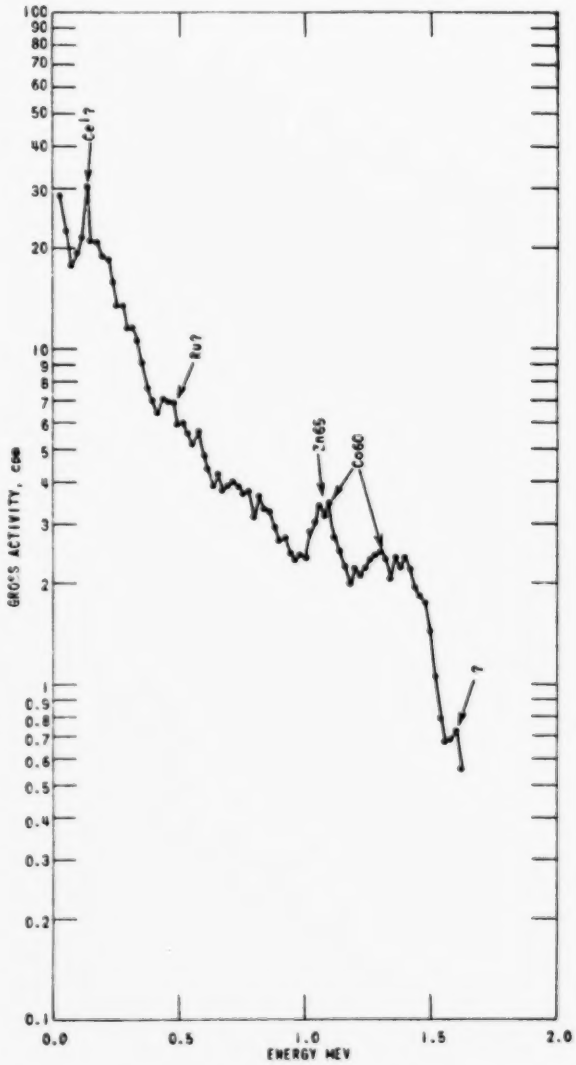

Figure 14. ALGAE FRACTION R-4

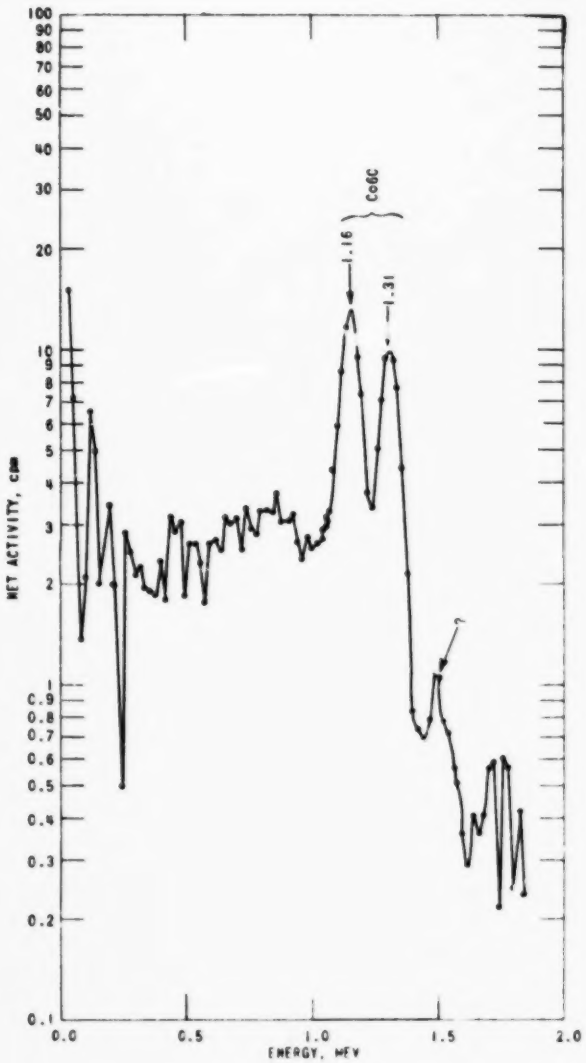

Figure 15. ALGAE FRACTION R-5

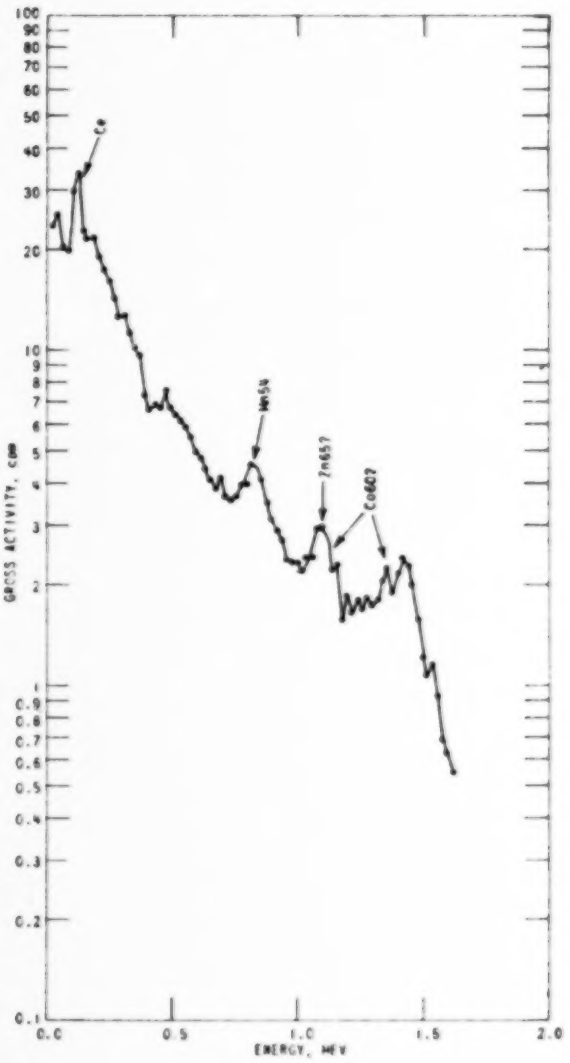

Figure 16. ALGAE FRACTION R-7

Figure 17. ALGAE FRACTION R-9, R-11

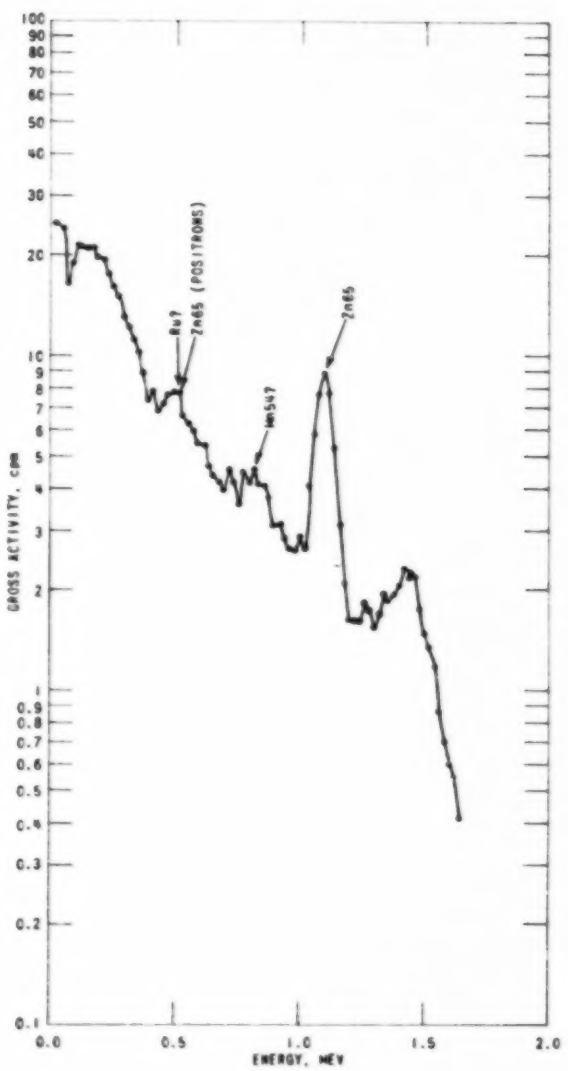

Figure 18. ALGAE FRACTION R-12

V. FATE OF RADIOACTIVE MATERIAL

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Albert H. Story, Assistant Sanitary Engineer
Michael Howell, Jr., Assistant Sanitary Engineer

1. INTRODUCTION

A sample of natural water collected from any locality in the United States—and quite possibly from any place in the world—will show contamination by radioactive materials. The sources of this contamination will be from deposits of naturally occurring radioactive materials and from man-made nuclides connected with the fissioning of uranium and plutonium. The naturally occurring radioactive contaminants are solubilized by the water as it passes over and through the soil after its deposition as rainfall while the man-made radionuclides may enter into the hydrosphere either as fallout resulting from nuclear weapons tests or from their introduction into bodies of water as low-level wastes from atomic energy installations or other facilities manufacturing, processing, or using radioisotopes.

The naturally occurring radioactive contaminants have been in natural waters in varying concentrations since the beginning and man has perhaps unconsciously adjusted his life to them. It is not meant to imply by this statement that these naturally occurring radiations are not harmful—in fact some of the alpha emitters among them can be most harmful if ingested—but at least they are present and little can be done easily to alleviate the danger from them. It is the damage from the newer sources, which may be excessive when added to that from the naturally occurring materials, which we must ponder and many stream studies have been undertaken to assay their concentration in the water environment. In each case these studies have shown a sharper decrease in gross water activities with time than can be explained on the basis of natural radioactive decay alone, indicating that environmental factors in the stream are aiding, at least temporarily, in the decontamination of the water phase.

As was stated previously, most of these stream studies which have been made indicate changes in radiation levels of the water on the basis of gross activity, neglecting almost entirely the fact that this attenuation of activity levels might be due to the selective removal of a specific isotope or of specific isotopes. It is for this reason that the effects of dilution and the chemical and biological aspects of precipitation, ion exchange, adsorption, absorption, assimilation, or metabolism on specific nuclide contaminants must be ascertained before we can predict, with a reasonable degree of accuracy, the ultimate disposition in space and time of radioactive waste materials which find their way into a natural stream.

It is the purpose of this research project to determine the various physical, chemical and biological effects that the water environment exerts on added radioactive contaminants so that by use of this knowledge we can better assess the public health dangers which may arise from a radioactive waste disposal program and consequently to determine the extent to which a given stream may be used as a means of disposal and dispersal of radionuclides consistent with rational public health standards.

2. KNOLLS ATOMIC POWER LABORATORY STUDIES

The analyses of samples collected prior to the beginning date of this report were completed and the results reported to the Knolls Atomic Power Laboratory for their review. The analytical data included the concentration levels of specific nuclides as well as gross alpha, beta, and gamma results. With this report was forwarded a request for additional samples.

In August, 60 samples were received. These samples were collected at three points on the Mohawk River: 1) three miles upstream from the point of effluent discharge; 2) at the effluent discharge outlet; and 3) one and seven tenths miles downstream from the point of effluent discharge. Each sample represented a collection from one of the stations for a period varying from one to several days. The waste effluent samples were composited continuously at a rate proportional to discharge flow, while the others were grab samples.

Aliquots of the effluent discharge samples from July 15 to July 21, 1958, inclusive, were analyzed for gross beta, cesium-137, strontium-90, and strontium-89. Table 4 shows the results of these analyses.

In the analytical treatment of these samples conventional radiochemical techniques were used, with the exception of the analyses for strontium and cesi-

Table 4. RADIOCHEMICAL ANALYSES - KAPL EFFLUENT SAMPLES

Date of Collection	7/15	7/16	7/17	7/18	7/19-7/21
Cs^{137}*, μμc/l	8,700	8,400	9,200	9,150	6,100
Sr^{90}, μμc/l	7,200	5,320	5,000	6,940	4,370
Sr^{89}, μμc/l	200	158	--	--	45
Others**	4,689	1,290	2,440	2,890	1,370
Total	20,780	15,168	16,640	18,980	11,885
Gross β, μμc/l	21,850	15,450	13,760	15,880	11,200

* Assuming 25% gamma counting efficiency for point source on 4" NaI (Tl) crystal.
** Value obtained by counting an aliquot of supernate after removal of strontium and cesium.

um. In these two instances, certain refinements in usual methods of determination were made to improve counting efficiencies. (See Section III)

The gross beta activities of the five effluent samples processed ranged from 11,000 μμc/liter to 22,000 μμc/liter. Eighty to ninety per cent of the activity was contributed by the cesium-137 and strontium-90, the cesium activity being somewhat in excess of the strontium activity. Gamma scans of these effluent samples showed good cesium-137 peaks with some indication of the presence of cerium-144 and possibly iodine-131.

Since the processing of daily samples places a heavy load on the radiochemistry section, it was decided after a visit to KAPL in August to composite individual samples from each collection station weekly for gross alpha and beta activity determinations in both the dissolved and suspended solids fractions and to combine weekly composites into four-week composites for radionuclide analyses.

The radiochemical data on samples collected and composited in accordance with this new schedule are shown in Table 5.

Table 5. GROSS ACTIVITY DATA ON KAPL SAMPLES

Week	Sample	Vol., ml	Suspended			Dissolved		
			mg/l	cpm*	μμc/l	mg/l	cpm*	μμc/l
7/15-21	Upstream	500	6	1.1	1.6	162.0	5.7	10.9
	Effluent	100	-	---	---	333.0	2511	19,400
	Downstream	500	5.2	1.3	1.9	183.2	25.8	52.2
7/21-27	Upstream	500	4.6	1.8	2.6	170.0	6.3	12.3
	Effluent	100	13.0	132	965	340.0	2286	17,800
	Downstream	500	5.0	0.7	1.0	170.0	9.4	18.4
7/28-8/4	Upstream	500	8.0	2.4	3.5	174.0	9.3	18.2
	Effluent	100	25.0	129	942	351.0	1413	11,000
	Downstream	500	140	11.4	28	148.0	6.0	11.2
8/4-10	Upstream	500	14.0	---	---	180.0	10.5	20.6
	Effluent	100	19.0	48	350	350.0	1039	8,100
	Downstream	500	5.0	1.1	2.0	170.6	12.9	25.0
8/11-17	Upstream	500	14.0	3.6	5	179.6	20.3	40
	Effluent	100	19.0	---	---	320.0	1485	11,400
	Downstream	500	0.0	0.4	1	173.2	4.8	9

* These data are based on the individual sample volumes indicated.

Table 5. (Continued)

Week	Sample	Vol., ml	Suspended			Dissolved		
			mg/l	cpm*	μμc/l	mg/l	cpm*	μμc/l
8/18-24	Upstream	500	9.0	1.5	2	190.0	10.8	22
	Effluent	100	8.0	120.6	880	334.0	1657	12,700
	Downstream	500	0.2	35.5	50	174.0	7.7	15
8/25-31	Upstream	500	12.8	4.5	7	207.0	5.1	11
	Effluent	100	27.0	11.9	87	361.0	639	4,900
	Downstream	----------	▷	not	received	◁	----------	
9/2-7	Upstream	500	19.6	0.6	1.0	193.2	6.8	14
	Effluent	100	41.0	36.7	268	311.0	2317	17,700
	Downstream	500	13.0	2.0	2.9	195.6	71.5	144
9/8	Upstream	500	12.8	---	---	193.4	25.1	50.7
	Effluent	100	68.0	7.4	5.4	324.0	650	5,080
	Downstream	500	59.0	2.6	4.9	182.0	11.4	22.4
9/15	Upstream	500	47.0	---	---	208.6	14.2	26.9
	Effluent	100	151.0	53.2	422	218.0	1399	10,050
	Downstream	500	25.8	3.2	5.0	150.6	13.1	24.4
9/22	Upstream	500	9.0	0.1	0.15	206.4	28.9	60.1
	Effluent	100	136.0	12.7	98.4	269.0	530	3,980
	Downstream	500	58.2	3.3	6.2	148.4	12.2	22.7
9/29	Upstream	500	62.6	2.4	4.6	188.6	26.1	52.8
	Effluent	----------	▷	not	received	◁	----------	
	Downstream	500	21.8	3.4	5.2	149.0	29.5	54.9
10/6	Upstream	500	17.6	---	---	211.8	---	6.2
10/13	Upstream	500	22.2	---	---	197.2	---	6.1
10/20	Upstream	500	41.0	---	0.8	181.6	---	4.3
10/27	Upstream	500	97.4	---	7.3	234.2	---	21
11/3	Upstream	500	66.2	---	8.2	335.8	---	13
11/10	Effluent	500	37.6	---	60	251.4	---	2,950
	Upstream	500	96.6	---	8.0	157.2	---	12
11/17	Upstream	500	110.6	---	14	164.8	---	20
11/24	Upstream	500	94.0	---	15	223.6	---	19
3/2	Downstream	500	17.2	1.8	2.4	133.2	2.5	4.3
3/9	Downstream	500	10.4	2.4	3.2	144.2	7.5	13.3
3/16	Downstream	500	11.6	3.1	4.2	124.6	6.7	11.5
4/6	Effluent	100	158	277	2230	491	1027	8,860
4/13	Effluent	100	155	321	2590	---	486	4,610
4/20	Effluent	100	68	196	1420	463	925	7,865

* These data are based on the individual sample volumes indicated.

Table 5. (Continued)

Week	Sample	Vol., ml	Suspended			Dissolved		
			mg/l	cpm*	μμc/l	mg/l	cpm*	μμc/l
4/27	Effluent	100	96	85	624	525	728	6,346
5/4	Effluent	100	158	214	1705	475	786	6,780
5/11	Effluent	100	209	213	1800	963	480	4,950
5/18	Effluent	100	150	308.4	2260	976	1357	13,570
	Downstream	500	---	0	0	---	0	0
5/25	Effluent	100	73	161.7	1100	540	849.5	6,500
	Downstream	500	---	0	0	56.4	1.9	3.0
6/1	Effluent	100	126	71.9	512	799	339	3,080
	Upstream	500	34.6	2.6	4.0	150.4	6.3	11.2
	Downstream	500	3.0	2.9	3.9	79.2	0	0
6/8	Upstream	500	17.6	0.7	1.4	157.4	5.7	10.4
6/15	Effluent	100	120	132.9	950	831	955.4	8,670
	Upstream	500	33.8	2.1	3.2	142	6.2	11.0
6/22	Effluent	100	67	765.8	5120	697	2293	20,800
	Upstream	500	---	0	0	255.8	5.4	11.4
	Downstream	500	22.6	2.0	28.2	191.8	5.6	10.8
6/29	Effluent	100	434	73.1	665	252	804.5	5,750
	Upstream	500	30.0	13.6	20.0	197.0	3.6	7.0
	Downstream	500	48.4	1.7	2.8	229.8	4.5	9.2

* These data are based on the individual sample volumes indicated.

Table 6. NUCLIDE ANALYSIS RESULTS OF 4-WEEK COMPOSITED KAPL SAMPLES

Sample		Suspended				Dissolved			
Type	Date	Cs^{137}	Sr^{89}	Sr^{90}	Basic Sulfide	Cs^{137}	Sr^{89}	Sr^{90}	Basic Sulfide
Upstream	7/15-8/10	0	0	4.7		4	5	5.4	
Effluent		120	20	2.9	220	8320	1100	3520	4140
Downstream		0	0	0	4	8	2	1.4	4
Upstream	8/11-9/7	0	0	0	2	5	10	0.9	3
Effluent		5		45		2900		1300	50
Downstream									
Upstream	9/8-10/3	0		0		2		1.1	1
Effluent									
Downstream									

The completed work on nuclide analysis of the composite 4-week samples are reported in Table 6.

The values of activity listed in Table 5 are reported as having been determined by counting on the internal proportional counter (IPC) (2π). However, the upstream and downstream samples collected 7/15-21 through 8/4-10 were in fact counted on the low level background beta counter (LBBC) and the results converted to that which would have been obtained on the IPC-2π counter by use of a conversion factor of 4.2.

The conversion factor 4.2 was obtained by counting two of the effluent samples on both the IPC-2π and LBBC counters. The results of these determinations were as follows:

Sample	IPC	LBBC	Ratio
100 ml (7/21-27)	2286 ± 30	519 ± 15	4.4 :1
100 ml (7/28-8/4)	1413 ± 24	358 ± 12	3.95 :1
		Average	4.2 :1

Thus, if all the LBBC values are multiplied by 4.2, we get values equivalent to 2π (IPC) counters, and these can be converted to $\mu\mu c/l$ values by using efficiency values for mixed fission products. This is not exact, but gives reasonable values.

The alpha counts show no difference between upstream and downstream samples, although there is a little alpha activity in all effluents except the suspended solids fraction of 8/4-10.

The data presented in Table 5 are shown pictorially in Figures 19, 20, and 21, the total activities of the upstream, downstream, and effluent sample being plotted against the date of collection. In Figures 20 and 21, the same data are plotted in such a manner as to make comparisons of the activities of the stream samples and effluent samples easier. As would be expected there is little correlation between the upstream and effluent samples and that correlation which does exist would of course be due to chance. Between the downstream and effluent samples a more definite correlation does exist as will be noticed from Figure 21; however, this correlation appears to be slight.

Figure 22 shows a Freundlich plot (x/m, the gross activity x in $\mu\mu c$ per milligram of suspended solids versus the gross activity of the solution in $\mu\mu c$/liter), of a portion of the data in Table 5. An examination of Figure 22 shows that little correlation exists between these two items.

Figure 23 shows a plot similar to that of Figure 22. However, the data plotted here are derived from samples which when received were placed on a window ledge and before radiochemical analyses were started each contained an algae growth. The algae thus contributed to the suspended solids—the exact percentage of the contribution, however, is not known.

The correlation here appears quite definite despite the lack of knowledge of the exact nature of the suspended solids. The line of best fit was found by the method of least squares and gave values in the Freundlich isotherm

$$x/m = Kc^{\frac{1}{n}}$$

of k equal to 1.52×10^{-10} and n equal to 0.361.

There is little definite information on the fate of radionuclides discharged in the KAPL effluent which may be deduced from the data presented in Table 6. The difficulties encountered in analysis of the radiochemical data may in part be laid to the fact that only one phase of the water environment is being sampled, i.e. the suspended solid phase, and the other pertinent environmental factors are being excluded in our present sampling program. In order to properly analyze stream data of the type presented in Table 6, chemical, physical, biological, hydraulic, hydrological, meteorological, and chronological data are necessary. For example, the exact time of collection of the samples would allow us to predict if the upstream and downstream samples are representative of the same slug of water or to determine if one of the sample might reflect meteorological or hydrological conditions which do not affect the other at the time of collection.

It will be noted from the curves in Figure 19 that in some instances the activities of the upstream samples are greater than the activities of the downstream samples. Such results are difficult to explain at this stage of the investigation. Whether the results are due to errors or whether such results may be expected under certain stream conditions is not now known. However, such results do indicate that much additional information will be necessary in the future in order to properly evaluate the radiochemical results.

At the present time a brochure is under preparation which outlines in detail the procedures which will be followed in pursuit of the answers to the fate of radionuclides discharged to a water environment.

3. KAPL - FIELD STUDIES

A field party from the Radiological Health Activities Program at SEC spent the period of June 15 through 23, 1959 collecting samples of environmental media from the Mohawk River in the vicinity of KAPL. This field party consisted of two sanitary engineers and one aquatic biologist.

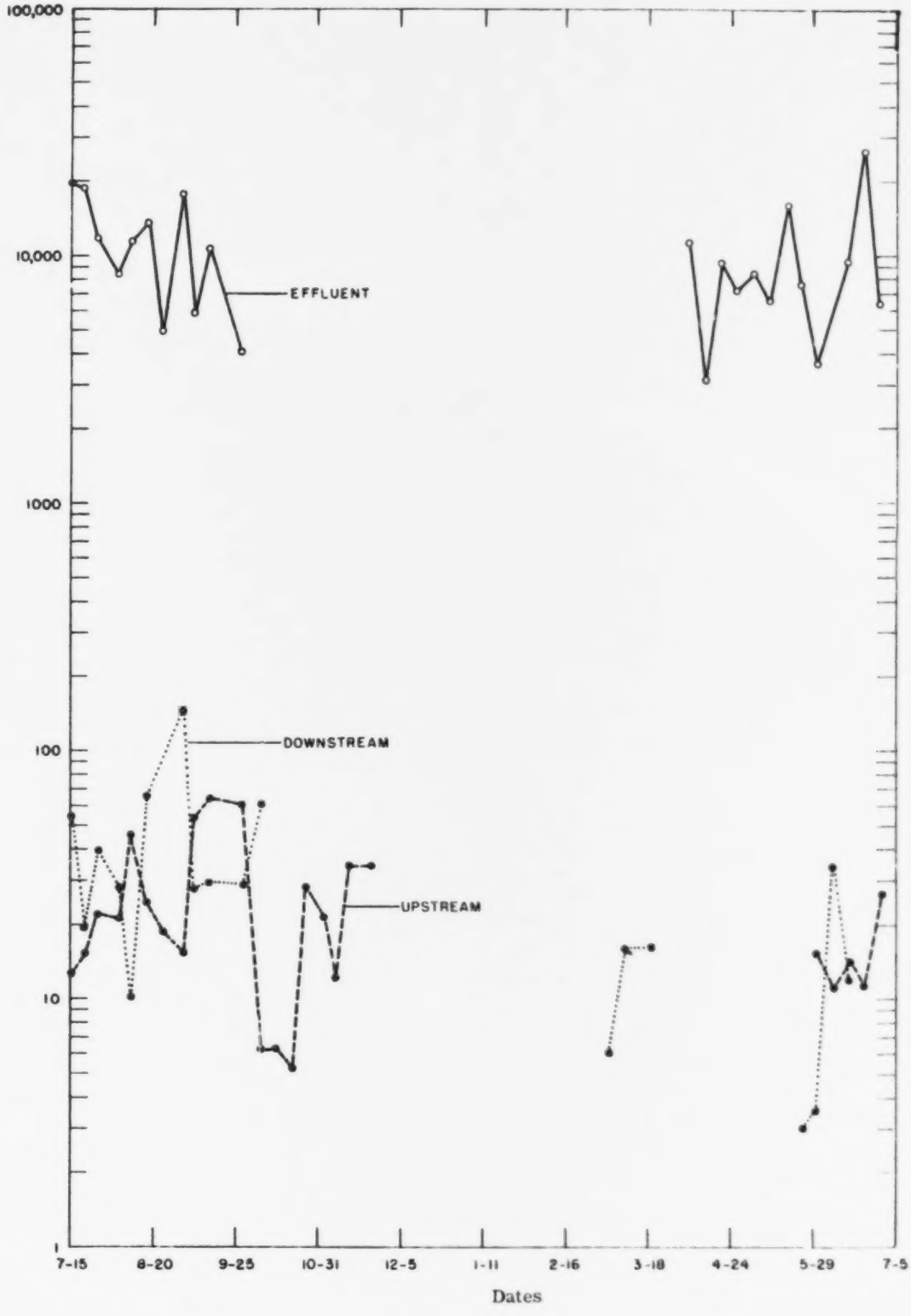

Figure 19. ACTIVITY IN MOHAWK RIVER, KAPL

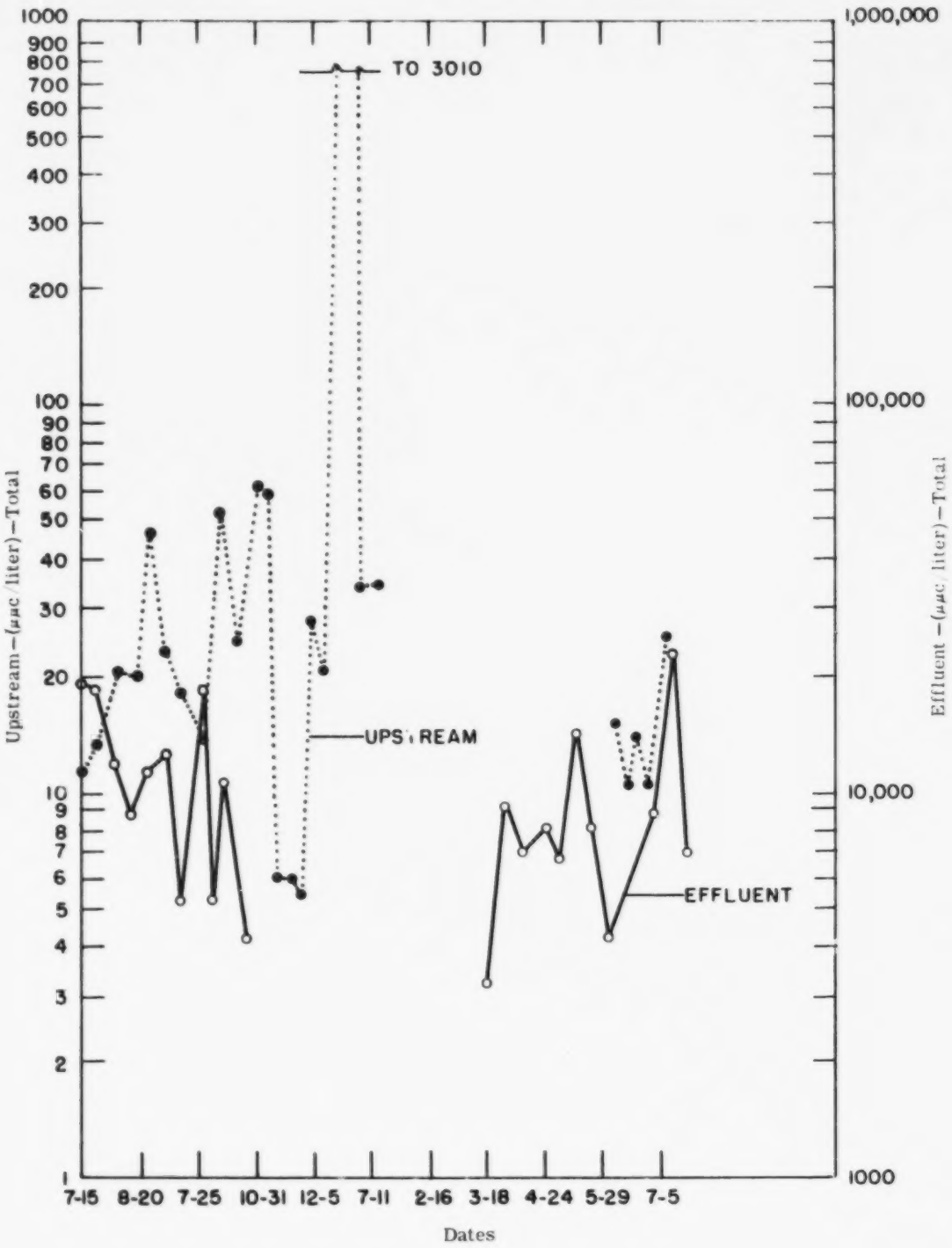

Figure 20. ACTIVITY OF KAPL EFFLUENT COMPARED TO UPSTREAM ACTIVITY

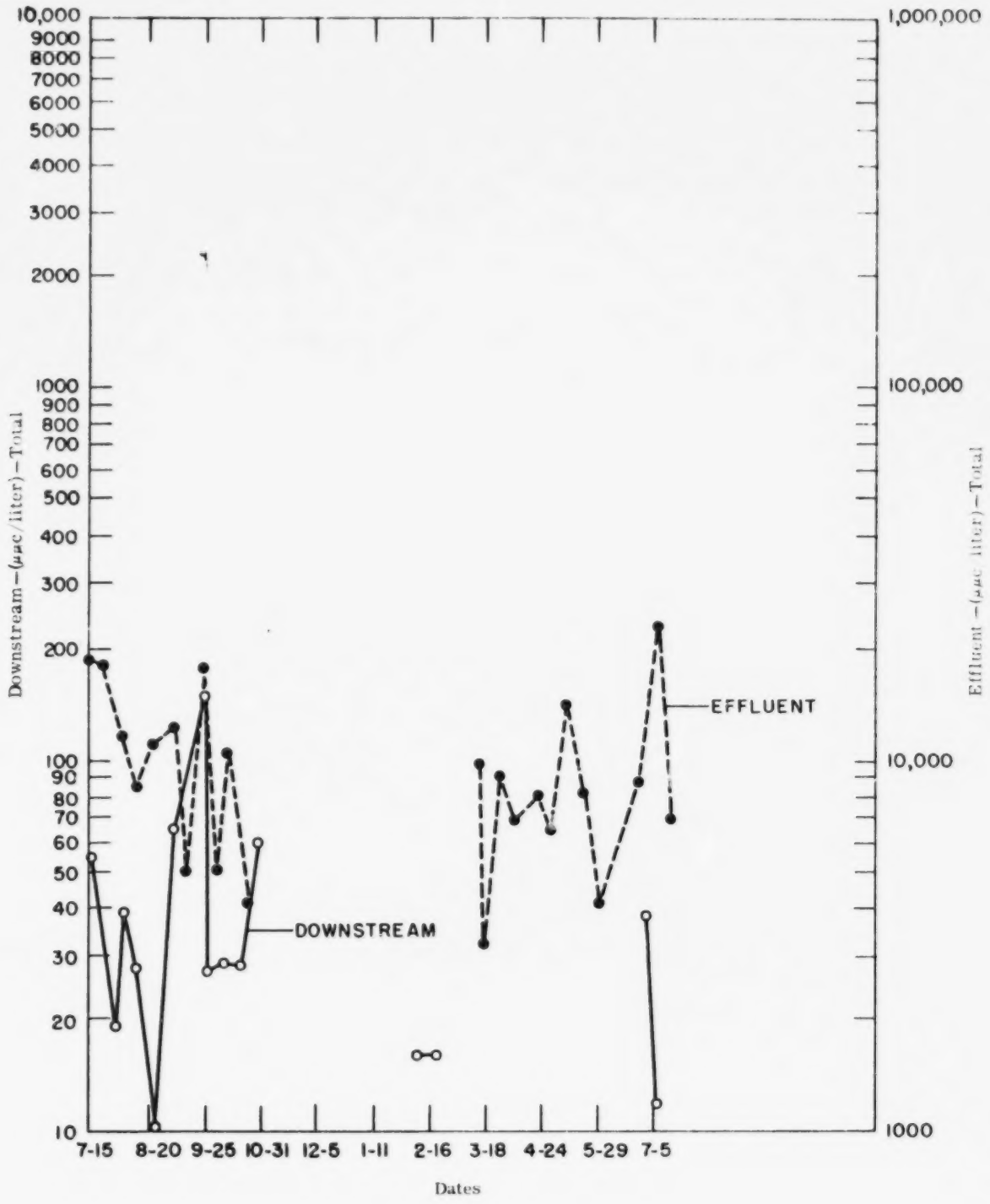

Figure 21. ACTIVITY OF KAPL EFFLUENT COMPARED TO DOWNSTREAM ACTIVITY

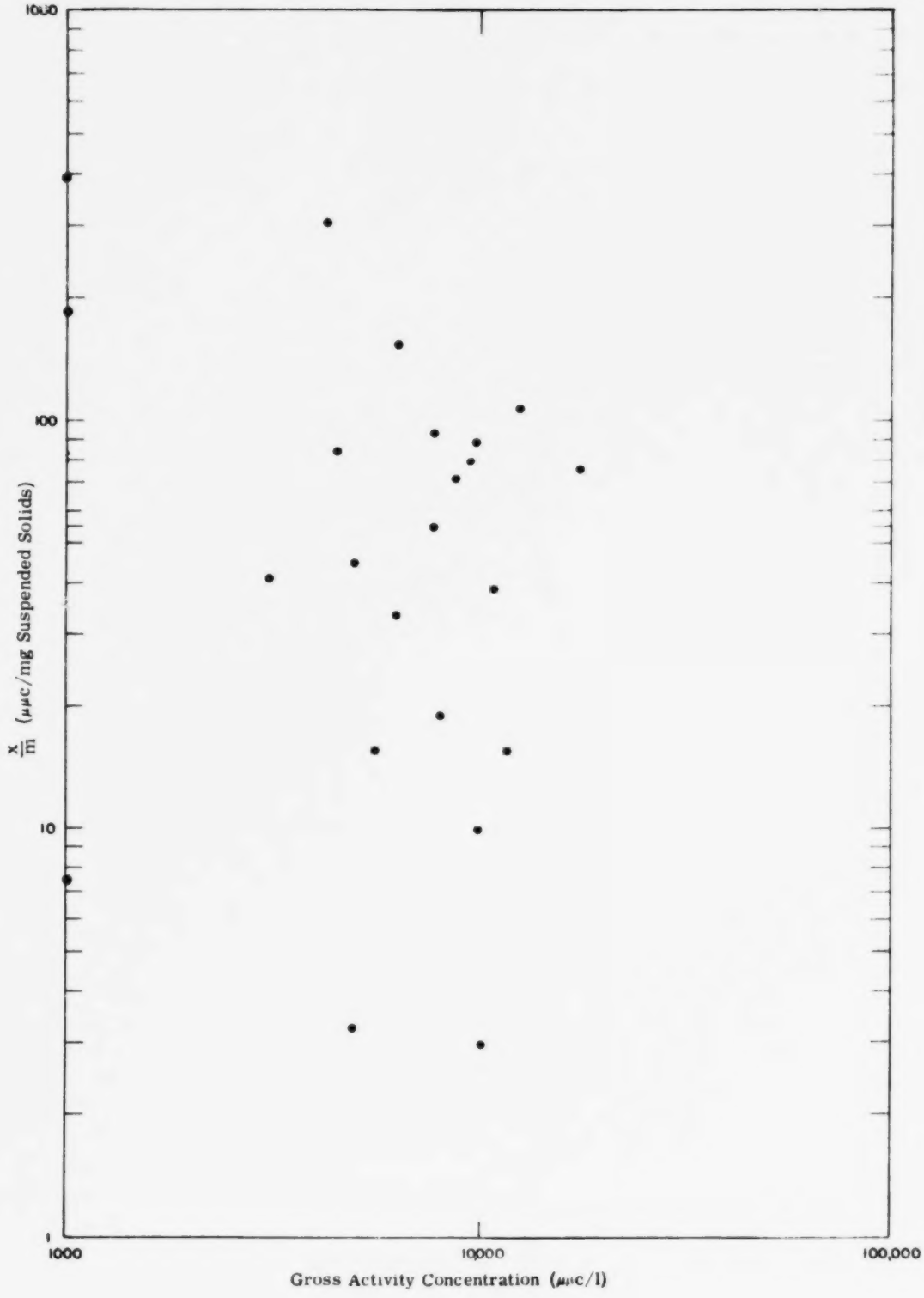

Figure 22. ACTIVITY OF SUSPENDED SOLIDS VS. ACTIVITY OF KAPL EFFLUENT

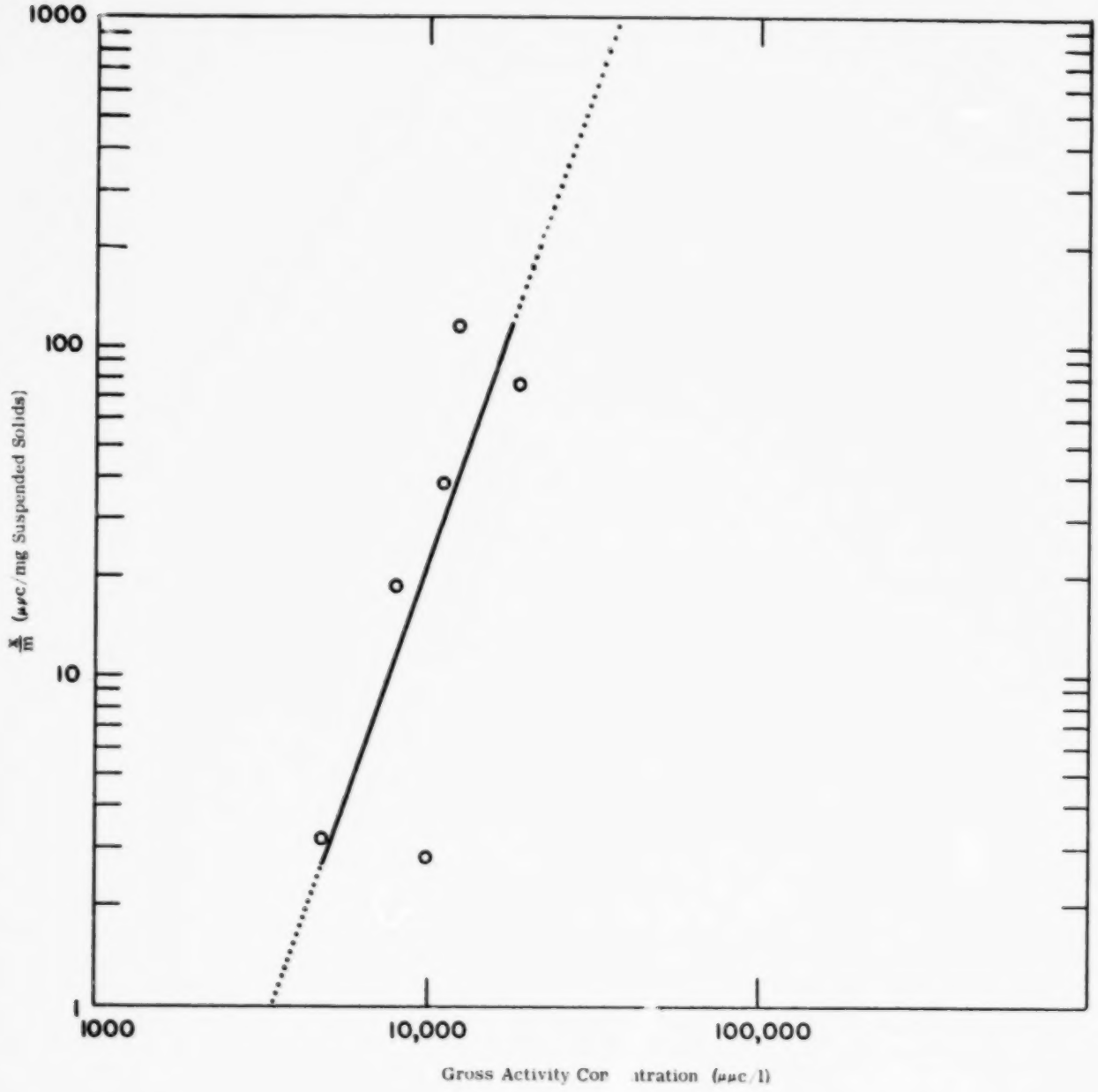

Figure 23. FREUNDLICH PLOT OF EFFLUENT SUSPENDED SOLIDS ACTIVITY VS. EFFLUENT ACTIVITY

During this period of time a rather comprehensive series of samples were collected. The inanimate samples included: 6 daily composite samples of KAPL effluent; 19 twenty-four hour composites of Mohawk River water collected at three points below the KAPL outfall; 2 samples each of Cohoes raw and filtered water; one rainwater sample; 7 bottom mud samples; and 2 rock samples (from river). Biota samples included: 4 plankton samples each collected by tows across the river at different points; 7 filamentous algae (mostly Clodophora) samples; 1 crayfish; 1 eastern painted terrapin; 1 sample of fresh water shrimp; 7 samples of juvenile fish representing 13 species; and 3 samples of adult fish representing 9 species.

In addition, 6 samples of a filamentous algae (Pithophora) were prepared at SEC and immersed at different points in the Mohawk River in order to investigate uptake and the possibility of using these as an indicator of radioactive pollution.

The analysis of these samples is now being done by the Radiochemical Section and upon completion a report of findings will be prepared.

4. SAVANNAH RIVER STUDIES

In July 1958, four water and two biological samples were received from the Savannah River Project. These samples were grab samples, two of which were collected from the Savannah River, one at Station 8 (the mouth of Steel Creek) and the other at Station 9 (Johnson's Landing) while the other two were collected one each from Steeds' Pond and Cassel Pond.

The results obtained following analyses of the water samples furnished by the Savannah River Plant are shown in Table 7.

Again no substantial conclusion can be drawn from the data presented in Table 7 as to the fate of nuclides discharged to a water environment, the difficulties encountered being the same as those met with in the KAPL samples.

The analysis of the biological samples collected from Steeds' Pond and Cassell Pond presents interesting and useful data. A gamma spectrum of the algae collected from Steeds' Pond was made on July 31 and several definite energy peaks were observed. The peaks at 0.49 and 0.74 Mev were identified as ruthenium-103 and zirconium-niobium-95, respectively. Two additional peaks were observed at 0.14 and 1.10 Mev and these were presumed to be cerium-144 and zinc-65, respectively. A gamma scan of the algae collected from Cassel Pond showed five definite peaks at 0.16, 0.50, 0.75, 1.10, and 1.29 Mev with two possible peaks at 0.32 and 0.64 Mev.

A similar gamma spectrum was obtained on the algae from Cassel Pond on October 21 and by a comparison of this spectra with the one obtained on July 31 (see Figure 11) it was possible to state that the nuclides cerium-141, cerium-144, chromium-51, ruthenium-103, ruthenium-106, zirconium-niobium-95, and cobalt-60 were definitely present; that the nuclides zinc-65, cesium-134, and tantalum-182 were probably present; and that the nuclides antimony-124, tin-113, and manganese-54 were possibly present.

In October, the algae sample from Cassel Pond was subjected to radiochemical methods of analysis in order to obtain the nuclides in a pure form for definite identification. As a result of this work, the presence of the isotopes definitely identified by means of the gamma spectra was confirmed as well as two of those tentatively identified, zinc-65 and manganese-54. Two of the nuclides provisionally identified previously, cesium-134 and antimony-124 were not found by this radiochemical analysis and the presence of tantalum-182 and tin-113 was left in doubt.

The results of these tests with algae taken from a contaminated water source seems to indicate that organisms of this type would serve as a valuable indicator of the presence of certain radioactive contaminants and further work along this line of investigation seems indicated.

Table 7. RESULTS OF RADIOCHEMICAL ANALYSES OF SAVANNAH RIVER WATER SAMPLES

Sample No.	Type	Weight mg/l	Gross alpha c/m/l	Gross beta c/m/l	Sr^{90} $\mu\mu c/l$
SR-1	Suspended	31.2	5.06 ± 1.28	29.4 ± 9.2	1.22 ± 0.78
	Dissolved	49.4	0.06 ± 0.60	42.4 ± 13.0	2.07 ± 0.75
SR-2	Suspended	61.0	8.8 ± 1.64	28.8 ± 8.8	0.52 ± 0.89
	Dissolved	41.4	1.20 ± 0.82	31.8 ± 8.6	5.80 ± 1.31
SR-3	Suspended	54.4	7.70 ± 0.96	37.2 ± 8.6	1.58 ± 0.70
	Dissolved	130.0	3.22 ± 0.96	36.2 ± 8.6	2.03 ± 0.74
SR-4	Suspended	17.2	1.32 ± 0.84	31.4 ± 8.6	1.32 ± 0.77
	Dissolved	52.0	0.48 ± 0.54	75.4 ± 9.6	3.10 ± 0.93

All errors are at the 95% confidence level.

The scheme used in the analysis of the algae sample from Cassel Pond is outlined in Figure 10 and spectra obtained are shown in Figures 11 to 18.

5. SHIPPINGPORT STUDIES

Four samples of approximately 4 liters each were received from the Shippingport area. These samples were collected on August 25 and 26, and September 3. Gross activity and tritium levels were determined and are reported in Table 2 on page 8.

Because the initial gamma spectrum obtained with 4 liters of 1 A Test Tank sample over the range 0-2 Mev was unsatisfactory, 2 liters of the sample were subjected to sulfide precipitation and the precipitate was counted. The spectrum indicated activity peaks at 0.08, 0.8, 1.13, and 1.3 Mev, corresponding respectively to Ta^{182} (0.08), Mn^{54} or Zr^{95} (0.8), and Co^{60} (1.13, 1.3). The latter radioisotope was confirmed by an energy summation peak at 2.50 Mev when the sample was scanned over the range 0-4 Mev.

6. STREAM SAMPLING DEVICE

A stream sampling device capable of fulfilling the following criteria was under development: 1) two liter capacity, 2) energy to collect sample to be supplied from environment, not from external power source, 3) reliable and maintenance-free operation, 4) variable sample collection depth, 5) rugged, shatter-proof construction, 6) continuous 24-hour composite sample, 7) flow-rate into samples to be proportional to flow-rate of stream, 8) inexpensive and readily available construction materials to be used, 9) quick change sample collector, and 10) not subject to freezing.

The development of a continuous sampling device which does not depend upon an electrical power source was initiated. The idea was to have a group of sampling bottles connected to a carboy full of water on a closed system then to evacuate the carboy by a syphon arrangement which would draw water into the sample bottles. After filling, the sample bottle was to have been isolated from the system by a rising ball float valve. At the present time a vacuum tank fitted with a needle valve to give the negative head is being considered in place of the syphon bottle arrangement. Problems which have arisen include the formation of a "water seal" in the tubing causing the flow to bypass a bottle; the influence of temperature changes on the pressure and, consequently, the rate of flow into a vacuum tank; and the fact that polyethylene bottles collapse under high vacuum thereby requiring the use of a stronger material for sampling bottles.

7. STREAM SAMPLER DEVELOPMENT

A stream sampler of extreme simplicity has been designed and constructed. In brief, the sampler consists of a one gallon plastic jug suspended in the stream about six inches under the water surface. Water inlet and air outlet tygon lines protrude from the jug stopper. The water inlet may be maintained at any elevation in the stream since the filling rate of the sampler is independent of the inlet's position and size. The air outlet, after passing through a desiccator, terminates above the water at an air orifice. The air release orifice has an opening 0.002 inches in diameter. In operation the amount of air in the collector is reduced by air flow through the orifice thus allowing the inflow of stream water. Due to the obstacles encountered in the production of the orifices, development of other types of samplers has been undertaken:

1. The design of an ion-exchange sampler is being completed. Such a sampler would have the advantages of a samll sample volume, thus eliminating lengthly evaporation procedures, and the achievement of a partial separation within the sampler.

2. A pressure driven sampler is being constructed which would sample a vertical cross section of a stream. The disadvantage of this type of sampler is that it is not self powered.

8. ACKNOWLEDGEMENT

The authors wish to acknowledge the work done by the Radiochemical Analyses Unit in performing the laboratory analyses.

VI. CONFERENCE

A two-day conference on "Nuclide Disposal to the Hydrosphere" was held at the Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, on the 5th and 6th of February, 1959. This conference brought together some of the leading experts in the field of radioactive waste disposal to streams. Dr. Albert G. Friend acted as Chairman at this meeting and the participants were:

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Oak Ridge National Laboratory
Oak Ridge, Tennessee

Mr. Y. Feige
Atomic Energy Commission
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Manager, Aquatic Biology
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Hanford Atomic Products
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The keynote statement of the conference was contained in the following statement entitled, "The Purpose of Stream Survey", which was prepared by the Chairman:

"It is my feeling that stream surveys should be designed with the following purpose in mind. Sufficient stream data should be collected, which when considered in conjunction with the pertinent hydrological, geological and meteorological data available, will yield answers to these two aspects of radioactive waste disposal to streams.

"The first is a public health aspect. Specifically, will the continued discharge of a radioactive waste of specified nuclide composition to a receiving stream create an unreasonable health hazard to the ultimate consumer of this contaminated water, regardless of whether this water is used directly by man or is only one step in the food chain of man. The second aspect is one of economics, i.e. is the stream in question being used to the fullest extent permissible, taking into account rational public health standards as well as industrial users downstream, as a means of disposal and dispersal of radionuclides in wastes. This second aspect is an important one. For example, the treatment and disposal at sea of low-level radioactive wastes from all atomic energy installations would be a very expensive procedure and economically could limit the research necessary for the development of nuclear energy for peaceful purposes.

"It is obvious from these few notes that the mere delineation of these two aspects of nuclide disposal to a stream raises questions which in the present state of knowledge in the field cannot be answered for the simple reason that an adequate definition of 'unreasonable health hazard' and 'use of a stream to the fullest extent permissible' is not possible.

"It is hoped that this present meeting may shed more light on these problems we face by bringing together the various disciplines at work in the field. And although definite answers may not be expected, perhaps the paths we must follow to a solution may be pointed out."

The statements and discussions at this conference were tape recorded and a transcript has been prepared. A copy of the transcript has been forwarded to each participant for editing of his remarks and the final draft will be published by the Center.